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# Atmospheric Benzene Emissions

PEDCo-Environmental, Inc.
Cincinnati, OH

Prepared for

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# ATMOSPHERIC BENZENE EMISSIONS

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

All major potential sources of atmospheric benzene emissions were reviewed and evaluated to develop a comprehensive national inventory. Emission sources are categorized as mobile, stationary and natural. Gasoline-powered motor vehicles represent by far the largest overall source. The more diverse stationary sources are categorized by production, consumption and storage and transport. Maleic anhydride production represents the largest known source in this category. Available process control techniques are also described and, whenever possible, the best control technology for specific sources is identified. A projected emission inventory for the base year 1985 has been developed from available emission factor data and market projections for all of the major source categories.

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# 1.0 EXECUTIVE SUMMARY

Documented data on atmospheric benzene emissions were reviewed and evaluated. In general, these data were relatively sparse for most facets of this study.

Because benzene is highly toxic and widespread in the atmosphere, it has been listed as a hazardous pollutant under Section 112 of the Clean Air Act. Available data indicate that benzene is minimally reactive photochemically; thus it must be assumed that benzene is essentially unchanged chemically in the atmosphere before reaching receptor sites.

Benzene is emitted to the atmosphere in large quantities, principally from automotive and industrial sources. Benzene is not only a significant component of motor gasoline, but also is used as an intermediate in numerous chemical processes and is a by-product of others. In 1976, it ranked thirteenth among chemicals produced in the United States, with an output of 10.6 billion pounds.

It is estimated that benzene emissions from known sources exceeded 540 million pounds in 1976. Table 1-1 lists by category the primary sources and their estimated emissions. Although these figures clearly point to gasoline-powered motor vehicles as the largest total emitter, dispersion analysis of emissions data indicates that some stationary sources may be causing the highest levels of population exposure.

Table 1-1. ESTIMATE OF 1976 BENZENE EMISSIONS

| Source | Emission estimates, million lb/yr |
|---|---|
| Gasoline-powered motor vehicles | 443.6 |
| Petroleum refineries | 4.1 |
| Coke-oven operations | 7.8 |
| Known processes using benzene as an intermediate | 60.0[a] |
| Storage and distribution of gasoline and benzene | 24.8 |
| Solvent operations | b |
| Other miscellaneous | 4.0 |
| Total known losses | 544.3 |

[a] Does not include aniline or cyclohexane production for which no emissions estimates were obtainable.

[b] Unknown.

Mobile sources emit benzene from engine exhausts and by evaporative losses. The emission rate is a direct function of the controls applied and of the benzene content of gasoline. Older automobiles (1975 and earlier models) emit much larger quantities of benzene than newer model catalyst-equipped cars. Estimates of the extreme upper and lower limits of auto emissions (518.5 million lb/yr and 166 million lb/yr) are crude because benzene emissions data on cars without exhaust controls are very limited. Further, it is difficult to estimate the benzene level in gasoline (a critical factor in estimating auto emissions) because that level varies greatly by geographical region, sources of crude oil, and season of the year.

Stationary sources of benzene emissions are diverse. Thus, these sources have been grouped into three categories: benzene production, other chemical manufacturing, and storage and distribution of benzene and gasoline. Petroleum refineries and coke-oven operations are the major benzene production sources; however, estimates of the magnitude of emissions from these sources are unreliable because of lack of documented emissions data. The generally poor vapor containment in coke-oven operations indicates that benzene emissions from this source may have a significant impact on local ambient concentrations. Although petroleum refineries provide far better containment, they may be a significant source of benzene emissions because of their size and number.

Maleic anhydride production, which uses benzene as the raw material, not only is probably the largest source of benzene emissions in the source category of other chemical production, but also is probably the largest stationary source. Table 1-2 lists the major chemical products in which benzene is used, with estimates of emissions from these sources during 1976.

In the subcategory of storage and distribution emissions (primarily gasoline evaporation), service stations appear to be the most important source, particularly because of the large number of stations in operation and their widespread distribution nationwide. The importance of this source is increasing with the trend toward self-service operations, which could lead to greater exposure of the general population. Again, the benzene content of the gasoline is an important variable affecting emissions from this source.

### Table 1-2. ESTIMATED BENZENE EMISSIONS FROM PRODUCTION OF CHEMICALS (million lb/yr)

| Product | 1976 |
|---|---|
| Nitrobenzene | 7.5 |
| Aniline | a |
| Ethylbenzene | 2.7 |
| Styrene | 6.5 |
| Maleic Anhydride | 34.8 |
| Cyclohexane | a |
| Cumene | 0.5 |
| Phenol | 1.7 |
| Chlorobenzenes | 5.3 |
| Detergent alkylates | 0.3 |
| Other nonfuel uses | 0.7 |
| Total | 60.0 |

[a] Unknown.

Total atmospheric benzene emissions in 1976 are estimated to have been 544.3 million pounds. They are projected to decrease to 232.1 million pounds in 1985 (see Table 1-3). Essentially all of this decrease results from the phasing out of vehicles without exhaust controls (from 443.6 million pounds in 1976 to 107.1 in 1985). Maleic anhydride production is expected to remain the major stationary source. It is likely that the use of benzene in solvent operations will be eliminated by 1985 as a result of compliance by industry with the Occupational Safety and Health Administration's proposed regulations for benzene use; thus, any benzene emissions from solvent operations will arise primarily from benzene impurities in other solvents. The emission factors used to project the 1985 estimates of emissions from stationary sources (Table 1-3) are based on 1976 market trend data in the respective industries.

In benzene production facilities and facilities that use benzene as a chemical intermediate, the recovery of vapors containing organic compounds is frequently practiced for economic reasons and therefore is considered a part of the process in addition to being a means of controlling air pollution. When required, more stringent control of benzene vapors can be achieved by incineration, adsorption, or other techniques.

Table 1-3. PROJECTIONS OF 1985 BENZENE EMISSIONS

| Source | Emission estimate, million lb/yr | Increase over 1976 estimate, % |
|---|---|---|
| Gasoline-powered vehicles | 107.1 | -76 |
| Petroleum refineries | 6.5 | +42 |
| Coke-oven operations | 9.3 | +19 |
| Benzene consumption processes | 79.9 | +33 |
| Storage and distribution of gasoline and benzene | 25.3 | + 2 |
| Other miscellaneous | 4.0 | + 3 |
| Total | 232.1 | |

## 2.0 INTRODUCTION

The purpose of this report is to establish an information base concerning sources of atmospheric benzene. Benzene is used widely throughout the United States in large volumes and in diverse applications. It is a clear, colorless, extremely flammable liquid that is highly toxic. For these reasons benzene has been classified as a hazardous pollutant under Section 112 of the Clean Air Act.

Benzene is a by-product of petroleum and coal. It is used as a component of gasoline, as a solvent, and as an intermediate in the production of numerous chemicals, including ethylbenzene, cumene, cyclohexane, nitrobenzene, maleic anhydride, chlorobenzene, and detergent alkylate.

Benzene is released to the atmosphere from a variety of mobile and stationary sources; principal emitters are gasoline-powered combustion engines, gasoline storage and distribution facilities, petroleum refineries, by-product coke ovens, and chemical and industrial operations that consume or handle benzene. No information is available concerning naturally occurring benzene emissions.

Information for this study was obtained from government publications (largely those of the U.S. EPA and NIOSH), technical journals, industry publications and documents, data from state agencies, PEDCo technical files, and personal contacts, all of which are cited as references. No data were generated by emissions tests or by tour of industrial facilities.

The scope of the study and the structure of this report are summarized as follows:

Evaluation of the chemical and physical factors affecting atmospheric benzene concentrations (Section 3).

Identification of the known primary sources of atmospheric benzene; with estimates of the benzene emissions from these sources (Section 4).

Review of the currently available techniques for control of benzene emissions from the major mobile and stationary sources (Section 5).

Projection of benzene production and consumption to the year 1985, with estimates of the 1985 emissions from the major sources (Section 6).

# 3.0 CHEMICAL AND PHYSICAL FACTORS AFFECTING ATMOSPHERIC LOADING

The atmospheric chemistry of benzene was reviewed to evaluate the possible impact of benzene emissions on ambient levels of photochemical oxidants and to identify possible secondary pollutants formed as a direct or indirect result of benzene oxidation. Benzene is not a normal atmospheric reaction product, therefore, the review was limited to consideration of the degradation of primary benzene emissions.

Factors affecting the atmospheric dispersion of benzene from major source categories were evaluated to identify atmospheric loading characteristics.

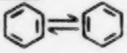
## 3.1 NATURAL SOURCES

No literature was found to indicate the likely major natural sources of benzene or their contribution to the total environmental benzene inventory. Benzene appears to be a relatively minor constituent of the total environmental burden of hydrocarbons from natural sources.

## 3.2 PHYSICAL AND CHEMICAL PROPERTIES OF BENZENE

Benzene is a clear, colorless, extremely flammable liquid with a distinct odor. It is sometimes called benzol, phenyl hydride, coal naphtha, phene, benzole, or cyclohexatriene. Table 3-1 presents selected chemical and physical properties of this compound.

Table 3-1. SIGNIFICANT PROPERTIES OF BENZENE[103,123,136]

| | |
|---|---|
| Formula | Chemical: $C_6H_6$ Structural:  |
| Molecular weight | 78.11 |
| Melting point | 5.51°C |
| Boiler point | 80.093° to 80.094°C |
| Flash point | -11°C (closed cup) |
| Specific gravity | 0.9894 at 20°C |
| Autoignition temperature | 538°C |
| Vapor pressure | 100 mm Hg at 26.1°C |
| Vapor density | 277 g/ml |
| Explosive limits | 1.4 to 6.8% by volume |
| Solubility | Very soluble in most organic solvents; slightly soluble in water (700 ppm at 20°C) |

## 3.3 ATMOSPHERIC REACTIONS

Lack of experimental data prohibits a comprehensive evaluation of benzene chemistry. Because of the low relative reactivity of benzene, gaseous reactions at ambient conditions have not received the attention given to benzene solution-phase chemistry. Very limited quantitative data are available concerning benzene reaction rates and degradation products.[24,156]

The relative reactivity of benzene and other hydrocarbons can be evaluated in several ways. Analysis of the influence of benzene on the rate of oxidation of nitric oxide (NO) to nitrogen dioxide ($NO_2$) is the most common. Since the generation of ozone ($O_3$) is proportional to the $NO_2/NO$ ratio,[24] this index provides an approximate measure of the ozone formation potential of hydrocarbons. Chemical reactivity also is measured by the relative rates of reaction with important oxidizing species such as hydroxyl radicals (OH), atomic oxygen [$O(^3P)$], and ozone. This index provides an approximate rate of formation of secondary degradation products. Data on reactivity of benzene and other hydrocarbon compounds (presented in Table 3-2) indicate that benzene is substantially less reactive than other common atmospheric hydrocarbons. For example, reactivity of benzene is one-tenth that of propylene and one-third that of n-hexane.

The reactivity relationships of benzene with alkyl-benzene compounds are consistent with electrophilic attack on the aromatic ring. The xylenes, trimethyl-benzenes, and tetramethyl-benzenes have reactivities one order of magnitude larger than that of unsubstituted benzene. The low apparent reactivity of benzene compared with that of all olefins, most aromatics, and most paraffins suggests that benzene does not participate significantly in photochemical oxidant formation in the immediate vicinity of the source. It is conceivable, however, that benzene could react during long-range transport of urban air masses. Data are inadequate for evaluation of the role of benzene relative to naturally generated unsaturated hydrocarbons and paraffins within the urban air mass.

The products of benzene reactions depend primarily on the types of oxidation agents available, since benzene does not absorb ultraviolet light in the ambient spectrum (Reference 23 gives benzene absorption-band data). The most important oxidizing species could consist of hydroxyl radicals, atomic oxygen, excited molecular oxygen, and ozone. Although the benzene decay paths and ultimate reac-

## Table 3-2. ATMOSPHERIC REACTIVITIES OF BENZENE AND OTHER HYDROCARBON COMPOUNDS[a]

| Compound | Based on NO oxidation | Based on hydrocarbon reaction | |
|---|---|---|---|
| | | OH | $O(^3P)$ |
| **Aromatics** | | | |
| Benzene | 0.10[62,124,156] | <0.05[124] | <0.01[124,156] |
| Toluene | 0.25[62,156] | N.D.[b] | 0.03[156] |
| p-xylene | 0.50[62,156] | N.D. | N.D. |
| o-xylene | 0.50[62,156] | N.D. | N.D. |
| m-xylene | 1.00[62,156] | 1.00[156] | N.D. |
| Ethylbenzene | 0.34[62] | N.D. | N.D. |
| 1,3,5 Trimethylbenzene | 1.50[62,156] | N.D. | N.D. |
| 1,2,3,4 Tetramethylbenzene | 1.00[62] | N.D. | N.D. |
| **Paraffins** | | | |
| Methane | 0.10[62] | <0.001[156] | <0.001[156] |
| Propane | 0.40[62] | 0.08[156] | 0.04[156] |
| n-Butane | 0.75[62] | 0.20[156] | 0.05[156] |
| n-Hexane | 0.93[62] | N.D. | N.D. |
| **Olefins** | | | |
| Ethylene | 0.50[62,156] | 0.2[124,156] | 0.2[124,156] |
| Propylene | 1.00 (basis) | 1.00 (basis) | 1.00 (basis) |
| Isobutene | 1.00[62,124,156] | 3.00[124,156] | 4.50[124,156] |
| Trans-2-butene | 3.50[62,124,156] | 4.10[124,156] | 5.50[124,156] |

[a] Values shown represent an approximate average of data in the references cited. The references are summary documents with citations to the original experimental work.

[b] N.D. - No data.

tion products have not been determined, the products probably include formaldehyde, peroxides, and epoxides.[24]

## 3.4 ATMOSPHERIC TRANSPORT

In analysis of the dispersion of benzene in the atmosphere after being released from a source, it is assumed that benzene disperses in much the same manner as an inert gas; i.e., it neither has any appreciable weight nor adds any buoyancy to the dispersing medium. Thus, the primary consideration should be the type of source from which the benzene is released and how it affects the plume rise.[155]

Gasoline-powered automobiles account for about 82 percent of the total nationwide emissions. However, this is not to say that approximately 82 percent of the measured, ambient benzene in any one area results from automobile emissions. Varying source characteristics and local meteorological conditions are the determining factors governing the benzene source-receptor relationships. The source-receptor relationships for three types of benzene sources [automobiles, point sources (e.g. maleic anhydride plants), and gasoline distribution] are discussed in the following paragraphs.

When considered collectively on a nationwide basis, automobiles constitute the largest source of benzene emissions; however, individually they are probably the smallest of the benzene emitters. It would be difficult to relate benzene emissions from individual automobiles to ambient air quality; therefore, the analysis is approached by considering total emissions from a length of highway. The emission rate then depends on the number of vehicles traveling along the designated length at any one time and the number of lanes in the highway.[114]

Ground-level concentrations of a gaseous pollutant (benzene) downwind of a highway depend on the orientation of the highway with respect to the wind direction. For example, downwind concentrations of benzene will be considerably less when the wind is moving perpendicular to the highway than when it is moving parallel to the highway. Because of their low emission height and horizontal exit velocities, benzene emissions from automobiles have greater impact close to the roadway than would emissions from an elevated stack.

Benzene emissions from maleic anhydride plants exhibit a different dispersion pattern than automobile emissions because the characteristics of the two sources differ, e.g. the height at which the emissions are released. Typical stack heights at maleic anhydride process plants are 60 to 100 feet, whereas automobile exhausts are essentially at ground level. Vertical exit velocities are generally much higher at a process plant, and the greater plume rise causes the pollutants to disperse to a greater degree. Because the benzene is emitted at a greater height, its maximum ground-level impact occurs further downwind from the source than that of emissions from an automobile.

Leaks in pump seals and valves are another source of benzene emissions within a maleic anhydride plant (and most other benzene-consuming processes). Since they have no appreciable vertical exit velocities or elevated temperatures, these sources are termed fugitive sources. They exert their greatest impact close to the source, probably within the plant boundaries. Collectively, the magnitude of fugitive source emissions probably approaches that of the process stack emissions and should be seriously considered in an analysis of the benzene problem.

Characteristics of the gasoline distribution sources, e.g. service stations, are very similar to those of automobiles when considered individually. Emissions occur essentially at ground level, and their exit velocities are very low. Unlike those from automobiles, however, emissions from gasoline distribution exit near-ambient temperatures and they occur at a stationary point. Benzene emissions from gasoline distribution have their greatest impact very close to the source and thus affect most strongly the persons working at these facilities.

Diurnal patterns also influence dispersion of emissions from the various sources. The process sources operate at a more or less constant level throughout the day, whereas automobile emissions undergo a definite diurnal cycle, peaking at the two rush-hour periods.[118] The diurnal pattern of emissions from gasoline distribution sources may closely resemble that of automobile emissions, at least the portion of the distribution emissions that occurs during filling of automobiles.

## 4.0 PRIMARY BENZENE EMISSION SOURCES AND LEVELS

In this section the known atmospheric benzene emissions are identified and, where possible, emission estimates and emission factors are presented. Sources are categorized as mobile and stationary. Table 4-1 presents estimated emissions from each source, identifies the report section describing the source and the estimated emission levels, and indicates the degree of accuracy of the emissions estimates. The accuracy estimates are subjective and are based upon PEDCo's evaluation of the available data.

### 4.1 MOBILE SOURCES

Gasoline-powered motor vehicles constitute the major source of benzene emissions in the United States. Aircraft, boats, off-road vehicles, construction equipment, motorcycles, and diesel-powered motor vehicles also emit benzene, but to a lesser degree. Gasoline-powered vehicles predominate because of their great numbers nationwide and the large quantities of gasoline they consume.[67] Table 4-2 summarizes estimates of benzene emissions from both gasoline- and diesel-fueled motor vehicles in 1976. Because of the lack of quantitative emission data, a range of emissions and a "best estimate" are presented for gasoline-powered motor vehicles.

## Table 4-1. ESTIMATED NATIONAL BENZENE EMISSION INVENTORY - 1976

| Source | Reference section in report | Emission estimate, $10^6$ lb/yr | Accuracy of estimate[d] |
|---|---|---|---|
| Mobile Sources | 4.1 | | |
| Gasoline-Powered Motor Vehicles | 4.1.1 | 443.6[a] | B |
| Diesel Heavy-Duty Vehicles | 4.1.2 | 3.8[a] | C |
| Other Mobile Sources | 4.1.2 | b | |
| | | | |
| Stationary Sources | 4.2 | | |
| Benzene Production | 4.2.1 | | |
| Petroleum refineries | 4.2.1 | 4.1 | C |
| Benzene purification | 4.2.1 | 0.2 | B |
| Coke oven operations | 4.2.2 | 7.8 | C |
| | | | |
| Benzene Consumption Processes | 4.2.3 | | |
| | | | |
| Nitrobenzene | | 7.5 | C |
| Aniline | | b | |
| Ethylbenzene | | 2.7 | C |
| Styrene | | 6.5 | B |
| Maleic anhydride | | 34.8 | A |
| Cyclohexane | | b | |
| Cumene | | 0.5 | C |
| Phenol | | 1.7 | B |
| Chlorobenzenes | | 5.3 | C |
| Detergent alkylate | | 0.3 | C |
| Solvent operations | | c | |
| Other nonfuel uses | | 0.7 | C |
| | | | |
| Storage and Transport | 4.2.4 | | |
| | | | |
| Gasoline storage | | 1.7 | B |
| Benzene storage | | 0.6 | B |
| Gasoline distribution | | 3.8 | B |
| Benzene distribution | | 2.0 | B |
| Crude oil operations | | 2.2 | C |
| Service stations | | 14.6 | B |
| | | | |
| - Known losses - | | 544.3 | |

[a] Source test data utilized in calculating benzene emissions.

[b] Unknown, relatively minor source.

[c] Unknown, potentially major source.

[d] Accuracy of estimate rating:

A - Good emission data available.
B - Fair estimate, ±100%.
C - Poor data base, order-of-magnitude estimate.

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Table 4-2. SUMMARY OF BENZENE EMISSIONS FOR TWO MOBILE SOURCE CATEGORIES, 1976
(Gg/year)

|  | Exhaust emissions | Evaporative losses | Total emissions |
|---|---|---|---|
| Gasoline-powered motor vehicles |  |  |  |
| Best estimate | 169.4 | 31.8 | 201.2 |
| Upper limit | 198.7 | 36.5 | 235.2 |
| Lower limit | 43.5 | 31.8 | 75.3 |
| Diesel-powered heavy-duty vehicles | 1.7 | N.A. |  |

N.A. Not available.

Emissions of benzene from gasoline combustion by motor vehicles are regulated indirectly by Federal standards that limit total hydrocarbon (THC) emissions from tailpipes and evaporative losses. The 1976 national (excluding California) hydrocarbon exhaust emission standard (0.93 g/km) for light-duty* passenger vehicles was lowered to 0.25 g/km for 1977/1978.[113,26] The national (excluding California) standard for light-duty trucks for 1976/1977 is 1.25 g/km.[113,26] The 1977 evaporative emission regulation for light-duty vehicles is 6 g/test by the SHED+ procedure.[151,26]

### 4.1.1 Emissions from Gasoline-Powered Motor Vehicles

This subsection presents a review of recent literature relevant to benzene emissions from gasoline-powered motor vehicles. These data form the basis for the benzene emission estimates presented in Section 4.1.2.

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* Vehicles rated at weighing 2.7 Mg (6000 lb) or less.[31]

+ Sealed Housing Method for Evaporative Determinations.

In 1974, total U.S. consumption of gasoline by highway vehicles was 365 $Mm^3$ (964 x $10^8$ gal). This figure includes private and commercial, Federal, civilian, state, county, and municipal usage.[67] Highway vehicles account for greater than 96 percent of the total gasoline consumption in the United States. Automobiles are the major consumer, but the category also includes light- and heavy-duty trucks.[67]

## Benzene Concentration in Gasoline

The benzene level in gasoline depends on numerous factors including the source of the crude oil, the geographic location of the source and the refiner, the grade of gasoline, the refinery operations, and the seasonal blends produced by each refinery. A report by the National Institutes of Occupational Safety and Health (NIOSH) on analysis of several different gasolines, based on 1976 data, shows an average benzene concentration of 1.24 liquid volume (lv) percent.[64] This value was determined by weighting averages of concentrations in the three grades of gasoline (premium, regular, and unleaded) from four commercial-brand service stations. Table 4-3 summarizes these data.

With the exception of alkylates and butanes, essentially all products manufactured for blending into finished motor gasolines contain benzene, in concentrations ranging from 0.5 to 8 volume percent.[22] Table 4-4 presents the benzene contents of gasoline blending components produced at two refineries. Both cautioned that their data on the benzene content of these individual streams are limited and should be considered as order-of-magnitude estimates.[22]

Table 4-3. SEASONAL BENZENE CONCENTRATIONS IN DIFFERENT BRANDS AND GRADES OF GASOLINE[39]

| Company (typical service station) | Gasoline grade | Volume of benzene in bulk sample, % | | Average volume of benzene, % |
|---|---|---|---|---|
| | | Summer | Winter | |
| Tresler-Comet | Premium | 1.11 | 1.10 | 1.11 |
| | Regular | 1.21 | 1.00 | 1.11 |
| | Unleaded | 1.41 | 1.60 | 1.51 |
| Bonded | Regular | 0.88 | 0.88 | 0.88 |
| | Unleaded | 1.19 | 1.60 | 1.40 |
| Bonded | Regular | 0.88 | 0.88 | 0.88 |
| | Unleaded | 1.20 | 1.60 | 1.40 |
| Clark | Regular | 0.97 | 2.00 | 1.49 |
| | Unleaded | 1.09 | 1.10 | 1.10 |

Table 4-4. BENZENE CONTENT OF GASOLINE BLENDING COMPONENTS[22]

| Stream | Refinery A | | Refinery B | Components[a] in complex refinery gasoline pool, volume % |
|---|---|---|---|---|
| | Average volume % in pool | Volume % benzene | Volume % benzene | |
| Heavy reformate | 30 | 1-7 | 0.5-1.5 | 29.0 |
| Raffinate[b] | | N.A. | 0.9 | 2.1 |
| Straight-run naphtha | 10 | 1-3 | 0.5-2.0 | 4.6<br>(nat. gaso.) |
| Pyolysis in gasoline[c] | >5 | 2-8[d] | 0.5-1.0[e] | None |
| Lt. fluid cat-cracked gasoline | 40 | 2-3 | 0.7-2.0 | 30.6 |
| Hvy. fluid cat-cracked gasoline | | <1-2 | 0.1-0.4 | |
| Hydrocracked gasoline[f] | | N.A. | 0.5-2.0 | 3.4 |
| Hydrocracked reformate[g] | | N.A. | 0.5-1.5 | |
| Butane | | 0 | 0 | 7.2 |
| Alkylate | | 0 | 0 | 12.5 |
| Coker gasoline | | | | 1.1 |
| Isomerized naphtha | | | | 9.5 |

[a] Arthur D. Little computer run for Texas Gulf Complex Refinery, 1985 (100 percent unleaded gasoline production).

[b] From benzene-toluene-xylene extraction.

[c] From steam cracking of gas oils.

[d] Assumes no benzene extraction.

[e] $C_5$ and $C_7$+ gasoline; assumes benzene extracted from $C_6$ gasoline.

[f] Light hydrocrackate is sent directly to gasoline.

[g] Reformed heavy hydrocrackate to gasoline.

Benzene content of commerical U.S. gasoline prior to 1974 was recorded as less than 1.0 lv percent. The maximum level in a single test sample was 1.3 lv percent.[121] A 1972 report on benzene analyses of 37 unleaded and low-lead gasolines from 15 companies in the United States showed a range from 0.3 to 2.0 percent benzene by volume, with an average of 0.8 percent.[19] Table 4-5 presents data on a series of gasoline samples obtained from domestic Gulf Oil refineries in October 1976. These data show an overall average of 1.25 lv percent in three grades of leaded gasolines. The highest value reported is 2.39 lv percent and the lowest, 0.54 lv percent.[122]

A nationwide survey during February/March 1977 showed benzene concentrations in gasoline ranging from 1.25 to 5 percent, with a national average of about 2.5 percent.[144] The survey indicates that benzene levels tend to be higher during winter than in other seasons. The investigators estimate that the benzene concentration in gasoline averages approximately 2 percent through the year. An American Petroleum Institute (API) study by duPont, will present a further survey of benzene levels in U.S. gasolines.[144]

For this report, the average value of 2 percent benzene in gasoline (from Reference 144) is used in emission estimates. At the present time no regulations are known to restrict benzene concentrations in gasoline.[142]

## Sources of Emissions from Gasoline-Powered Vehicles

Hydrocarbon emissions from gasoline-powered vehicles without emission controls originate from four sources: the carburetor, the fuel tank, the crankcase, and the engine exhaust. Hydrocarbons are generated from the carburetor by evaporation of fuel after a hot engine is shut off. Evaporation from the fuel tank occurs through vents in the tank and

Table 4-5. BENZENE LEVELS IN U.S. GULF OIL GASOLINES, OCTOBER 1976[122]

| Refinery source | Liquid volume of benzene, % | | |
|---|---|---|---|
| | Good Gulf | Gulf Crest | No-No$_x$ |
| A | 0.54 | 0.88 | 1.16 |
| B | 1.99 | 1.45 | 0.85 |
| C | 1.19 | 1.21 | 0.81 |
| D | 1.59 | 1.18 | 1.49 |
| E | 1.25 | 1.98 | 2.39 |
| F | 0.85 | 0.82 | 0.88 |
| Arithmetic mean | 1.24 | 1.25 | 1.26 |
| Standard deviation | 0.52 | 0.43 | 0.61 |

increases as the temperature in the tank increases. Crankcase emissions result from 'blowby' past the piston rings. 'Blowby' denotes leakage of the air/fuel charge into the crankcase during the compression power strokes in an internal combustion engine; these emissions, unless properly controlled, escape to the atmosphere through a vent tube or the crankcase ventilation cap. Crankcase losses were a significant source of hydrocarbon emissions in motor vehicles manufactured during the 1960's. Such emissions have been reduced in newer automobiles by venting the crankcase into the engine intake.[31] Hydrocarbon emissions in the engine exhaust gases result from incomplete combustion.[33] Available data indicate that research effort has been directed mostly towards control of hydrocarbon emissions from exhaust systems.

For our emission estimates, evaporative emission data for 1972 and older automobiles are taken from EPA Publication AP-42, Supplement 5, Table D.1-27.[31] Data for newer vehicles are taken from a 20-car study by Exxon Research and Engineering Corp., in which average hydrocarbon evaporative loss was measured at 8.7 g/SHED* test.[30] The sample included a cross section of 1973-75 cars with representative evaporative controls. Most of the evaporative loss occurs during the "hot soak" phase, which is estimated to contribute 85 percent of this total, or 7.4 g/test.[30] In our emission estimates, gasoline is assumed to contain 2 percent by volume of benzene and therefore benzene is assumed to constitute 2 percent of the hydrocarbon emission.+ With approximately 96 million cars* in current operation, benzene losses by evaporation would be 31.8 Gg/yr (70.1 million lb/yr).+

---

* Sealed Housing Method for Evaporative Determinations.

+ This assumption does not consider the relative volatility of benzene in the gasoline, which may result in some overestimation. Because of the variety of temperature and pressure conditions that must be considered in determining evaporative losses and because most emissions occur during "hot soak," which is at an elevated engine temperature, this assumption should not cause a significant overestimation.

Our estimates of total exhaust emissions are based on HC emission test data given in AP-42.[31] Benzene emission rates are presented below primarily to determine the benzene-to-THC ratio. These data are restricted almost entirely to catalyst-controlled vehicles, which have been in widespread use in the U.S. only since 1975. With few exceptions, the published data have not reported the benzene level in the gasoline under test conditions. Since this is a critical factor in estimates of benzene emissions, the usefulness of published studies is limited. Also, because certain components, such as ethylbenzene and other aromatics within the blend, can break down to form benzene, benzene can be emitted in engine exhaust even though it is nonexistent in the gasoline. Thus, benzene emissions depend not only on benzene levels in gasoline but also on particular characteristics of the gasoline blend.

Black and Bradow reported the benzene content of hydrocarbon emissions from engine exhausts of 10 automobiles.[17] These low-mileage vehicles included one 1972 production car with no catalytic emission control, three 1975 prototypes, and six 1975 production cars equipped with catalytic control devices. The cars were fueled from a single batch of unleaded test gasoline containing only 0.03 weight percent benzene. The vehicles were driven on a chassis dynamometer simulating a route typical of urban and highway driving conditions. Detailed hydrocarbon composition analysis (to determine benzene content) of exhaust samples was made by gas chromotography.[54] Results given in Table A-1 show hydrocarbon levels ranging from a high of 0.63 g/km (1.0 g/mile) to a low of 0.15 g/km (0.242 g/mile); these values conform to the expected effectiveness of exhaust controls. The highest benzene concentration among the catalyst-equipped cars was 9 mg/km (0.015 g/mile), whereas the concentration for the older uncontrolled 1972 vehicle was almost double that amount. The average benzene concentration was 2.3 percent of the total hydrocarbons.

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* Nationwide data from the Department of Transportation and the Motor Vehicle Manufacturers Association.

+ An average estimate determined from data on hydrocarbon emissions from controlled/uncontrolled vehicles.[95]

Olson Laboratories conducted benzene analyses of the exhaust from forty-five 1975 vehicles.[52] These data are presented in Table A-2. The mean benzene concentration was 9.94 mg/km (0.016 g/mile), with an average benzene-to-THC ratio of approximately 2.5 percent. The Olson study indicates a somewhat higher level of benzene exhaust emissions than the other studies mentioned and a wide variability in the data, with $\sigma$ equalling 0.018. Since these data are based on California vehicles and the benzene level in the test gasoline was not reported, they may not be representative on a nationwide basis.

Hydrocarbon emissions from a 1976 production vehicle using a lean burn system have been analyzed for benzene. Emissions were not significantly different ($\approx$0.0134 g/mile) from those from cars with catalyst systems. Benzene emissions from a 1974 production vehicle equipped with a thermal reactor system were similar to those of an uncontrolled vehicle. It is anticipated that to meet the more stringent hydrocarbon emission standards of the future, all highway gasoline-powered vehicles will be equipped with some type of catalyst system by 1985.

Our estimate of the benzene exhaust emissions in 1975-1976 (years in which catalyst control systems were installed on cars), utilizes a value of 1.0 g/mi of THC (from AP-42)[31] and a benzene-to-THC ratio of 0.025 (from the Olson studies) to arrive at an average level of 0.025 g of benzene/ mile. This benzene-to-THC ratio is based on data from the Olson studies for which no benzene level in the gasoline was reported. This level, although higher than the mean benzene emission rate of 0.016 g/mile from Olson (Table A-2), was chosen to reflect the impact of other control systems used on these vehicles and the effects of different engine conditions and gasoline benzene contents.

In 1973 the Bureau of Mines conducted a study[4] of vehicles with five different emission-control systems to explore the effects of fuel compositions and ambient temperature on exhaust HC emissions and benzene content. Five of six vehicles studied showed a decrease in benzene emission with decrease in fuel aromaticity. Ambient temperature tests indicated that the total hydrocarbon emissions and benzene emissions were lowest at 24°C; emissions increased at higher or lower temperatures, the most pronounced rate of increase occurring at lower temperatures. A more thorough review of this research is presented in Appendix A.

EPA is funding a number of catalyst characterization projects. Results of this work, to be available in 1978, should provide a more comprehensive data base concerning benzene emissions from auto exhaust.[52]

In summary, benzene content of gasoline is approximately 2.0 liquid volume percent, varying with the source of crude oil, refinery operations, grade of fuel, season, and geographic area. Whereas research concerning benzene emissions from vehicle evaporative sources has been limited, much effort has been directed towards analysis of tailpipe emissions. Studies confirm that benzene emissions from controlled vehicles are lower than those from uncontrolled vehicles. Also, tests show that an increase in fuel aromaticity is associated with an increase in benzene emissions. This emission increase, however, may not result from altered chemical composition but rather from changes in physical properties of the fuels and failure to adjust the vehicles for use of fuels of higher aromatic content. Studies also reveal that altering ambient temperatures in either direction from 24°C (simulating seasonal variations) increases benzene content of exhaust emissions. Tests at temperatures below 24°C generally produced higher benzene emissions than tests at temperatures above 24°C.

### 4.1.2 Benzene Emissions Calculations

Table 4-6 shows the information used to calculate the total 1976 benzene emissions from autos.

4.1.2.1 Best Estimate - Best estimate of 1976 auto emissions = exhaust plus evaporative losses.

$$\begin{aligned}
\text{Exhaust emissions} &= (96 \times 10^6)^{*}(9494)^{+}\ \Sigma\ a \times b \times c \\
&= (96 \times 10^6)(9494)(0.186) \\
&= 169.4 \text{ Gg/yr } (373.5 \text{ million lb/yr}). \\
\text{Evaporative losses} &= (96 \times 10^6)(9494)(0.02)^{\S}\ \Sigma\ a \times d \\
&= (96 \times 10^6)(9494)(0.02)(1.744) \\
&= 31.8 \text{ Gg/yr } (70.1 \text{ million lb/yr}). \\
\text{Total emissions} &= 201.2 \text{ Gg/yr } (443.6 \text{ million lb/yr}).
\end{aligned}$$

4.1.2.2 High Estimate - The high estimate of benzene emissions assumes that (1) no catalyst exhaust controls are used (exhaust emissions remain at the 1974 level, column $b_2$ Table 4-6) and (2) evaporative losses remain at the 1972 rate, as

---

[*] Estimated number of autos in operation in 1976.[95]

[+] Average mileage traveled per car in 1974.[95]

[§] Average fraction of benzene in gasoline.[144]

Table 4-6. AUTOMOBILE EMISSION FACTORS

| | | Exhaust emissions* | | | | | Evaporative losses |
|---|---|---|---|---|---|---|---|
| | | a | b | c | $b_1$ | $b_2$ | d |
| Vehicle model year | Vehicle age, years | Fraction of miles traveled+ | HC emissions,* g/mi | Benzene-to-HC ratio§ | Low HC emissions case** g/mi | High HC emissions case g/mi | HC g/mi |
| 1976 | 1 | 0.116 | 1.0 | 0.025 | 1.0 | 3.8 | 1.24 |
| 1975 | 2 | 0.135 | 1.2 | 0.025 | 1.2 | 3.8 | 1.24 |
| 1974 | 3 | 0.125 | 3.8 | 0.041 | 1.4 | 3.8 | 1.24 |
| 1973 | 4 | 0.122 | 4.1 | 0.041 | 1.6 | 4.1 | 1.24 |
| 1972 | 5 | 0.106 | 4.4 | 0.041 | 1.8 | 4.4 | 1.76 |
| 1971 | 6 | 0.086 | 5.5 | 0.041 | 2.0 | 5.5 | 1.78 |
| 1970 | 7 | 0.083 | 6.8 | 0.041 | 2.2 | 6.8 | 2.53 |
| 1969 | 8 | 0.072 | 6.8 | 0.041 | 2.4 | 6.8 | 2.53 |
| 1968 | 9 | 0.051 | 8.6 | 0.041 | 2.6 | 8.6 | 2.53 |
| 1967 | 10 plus | 0.105 | 9.1 | 0.041 | 2.8 | 9.1 | 2.53 |
| | | 1.000 | | | | | |

* All emission data are based on low-altitude, nonCalifornia cases.

+ AP-42, Supplement 5, Table 3.1.2-5
AP-42, Supplement 5, Table D.1-1, reference year 1976.

§ Ratios for 1975 and 1976 are based on experimental data; ratios for other years are based on noncatalyst levels.[13]

** Catalyst-controlled emissions are based on a 1976 base year rate of 1.0 g/mi and deterioration increases from AP-42, Supplement 5, Tables D.1-5 to D.1-1-17.

presented in AP-42[31] (designated as $d_1$). The benzene-to-HC ratio is assumed to be constant (0.041) for all model years.

Exhaust emissions $= (96 \times 10^6)(9494)(0.041)\ \Sigma\ a \times b_2$
$= (96 \times 10^6)(9494)(0.041)(5.32)$
$= 198.7$ Gg/yr (438.1 million lb/yr).

Evaporative losses $= (96 \times 10^6)(9494)(0.02)\ \Sigma\ a \times d_1$
$= (96 \times 10^6)(9494)(0.02)(2.00)$
$= 36.5$ Gg/yr (80.5 million lb/yr).

Total emissions $= 235.2$ Gg/yr (518.6 million lb/yr).

4.1.2.3 Low Estimate - The low estimate is based on all auto exhaust emissions at the 1976 catalyst-controlled level (column $b_1$ Table 4-6). Increases in exhaust rate with age of vehicle are because of catalyst deterioration and are based on AP-42 data.[31]

Exhaust emissions $= (96 \times 10^6)(9494)(0.025)\ \Sigma\ a \times b_1$
$= (96 \times 10^6)(9494)(0.025)(1.909)$
$= 43.5$ Gg/yr (95.9 million lb/yr).

Evaporative emissions (from subsection 4.1.2.1)
$= 31.8$ Gg/yr (70.1 million lb/yr)

Total emissions $= 75.3$ Gg/yr (166.0 million lb/yr).

4.1.2.4 Benzene Emission Variations - The best estimate of total benzene emissions from automobiles (see Table 4-2) is 201.2 Gg/yr (443.6 million lb/yr). The high and low estimates are 235.2 Gg/yr (518.6 million lb/yr) and 75.3 Gg/yr (166 million lb/yr). These high and low estimates are intended to indicate an overall emissions range and were derived by using extreme values for the emission factors. The effect of benzene in the gasoline on the benzene emission rate is not well-defined for either catalyst-controlled or precontrol vehicles. Also, the emission changes attributable to control method and vehicle age (deterioration rate) have not been tested adequately. Benzene emissions also may vary widely as a result of fractions of benzene and other aromatics in gasolines from different geographic regions in the United States (possibly an important factor in determining the levels of benzene to which specific populations are exposed).

### 4.1.3 Calculation of Emissions from Other Mobile Sources

Diesel-fueled engines and aircraft are not considered potentially large benzene emission sources. Diesel-fueled engines include power buses, light- and heavy-duty trucks, and some automobiles. Also included are locomotives; military, pleasure, and commercial vessels; and agricultural and heavy-duty-construction equipment. Total hydrocarbon emissions from diesels are relatively low because compression-ignition engines generally provide fairly complete combustion.[33] Crankcase and evaporative emissions are low, and the exhaust system is the only major hydrocarbon emission source.[33] Studies conducted by Southwest Research Institute on emissions of benzene and other volatile hydrocarbons from a heavy-duty diesel truck engine indicate a benzene-to-THC mean ratio of 0.0073 under varied engine stress conditions.[52] Table 4-7 presents data from this study. By use of this factor, a value for national benzene emissions from heavy-duty diesel trucks (assumed to be the greatest contributors of benzene in the category of "other mobile sources") is estimated as follows:

$$(9{,}630{,}754{,}000 \text{ gal.})^{*}(5.1 \text{ miles/gal.})^{+}(4.6 \text{ g/mile})^{\S}(0.0073) = 1.7 \text{ Gg benzene.}$$

---

[*] The total 1975 diesel fuel consumption in the United States.[141]

[+] Reference 63.

[§] Reference 31.

Table 4-7. BENZENE AND HC EMISSIONS FROM DIESEL ENGINE UNDER VARYING OPERATING CONDITIONS[52]

| Engine condition | Hydrocarbons, ppm C | Benzene, ppm C | Benzene/hydrocarbon, % |
|---|---|---|---|
| Intermediate speed, 2% load | 101 | 1.0 | 0.99 |
| Intermediate speed, 50% load | 89 | 0.5 | 0.56 |
| Intermediate speed, 100% load | 100 | 0.7 | 0.70 |
| High speed, 2% load | 92 | 0.7 | 0.76 |
| High speed, 50% load | 111 | 0.9 | 0.81 |
| High speed, 100% load | 85 | 0.9 | 1.06 |
| Idling speed, 2% load | 141 | 0.3 | 0.21 |
| Mean = | 102.7 | 0.7 | 0.73 |

It is anticipated that additional data on benzene emissions from diesel trucks (resulting from recently initiated EPA contracts) will be available in early 1978.[52] During a study of occupational exposure to benzene at service stations, NIOSH was unable to detect benzene in diesel fuel samples taken from survey sites.[64] Measured concentrations were reported to be below the detectable limit range of 0.5 liquid volume percent. Shell Oil reports that the benzene level in diesel fuel should be in the parts-per-million range because of flash point specifications.[43]

Although no data are available, the greatest potential for benzene emissions from aircraft probably occurs during ground operations (taxiing and idling after landing and before takeoff) when hydrocarbon emissions are most significant.[31]

## 4.2 STATIONARY SOURCES

The primary U.S. stationary sources of atmospheric benzene emissions are petroleum refineries, petrochemical plants, and coal coking operations. The projected breakdown of 1977 benzene production is as follows: 50 percent from refinery reformate, 16 percent from pyrolysis gas olefin streams, 5 to 8 percent from coking operations, 27 percent from hydrodealkylation of toluene, and 4 percent from imports.[51] The estimated volume of benzene production for 1977 is 1.56 billion gallons (5.6 $Mm^3$).[51]

Variations in benzene production from year to year reflect not only changes in petrochemical demands for benzene but also increases in gasoline demand. One of the effects of this demand is that refineries divert more aromatics to the gasoline pool to meet octane requirements, especially with the phasing down of lead antiknock additives.

Major benzene emission sources, addressed individually in the following sections, include petroleum refineries, coke ovens, major benzene consumption processes, and storage and distribution evaporative sources. Some minor sources are also discussed.

### 4.2.1 Petroleum Refining and Benzene Production

Petroleum refineries appear to represent a significant source of benzene emissions, although the emissions have never been quantified. Figure 4-1 presents the geographical distribution of U.S. refineries, and Appendix B-1 lists the refineries, with crude capacities and gasoline output. Major refinery products of interest here are commercial grades of benzene and gasoline. Appendix B-2 presents a list of U.S. producers of petroleum-based benzene, their locations, and their capacities; Figure 4-2 presents the geographical distribution of these facilities in the United States. These facilities are mostly along the Texas-Louisiana coastline of the Gulf of Mexico.

Benzene emission sources in refineries include (1) process emissions from light and heavy naphtha streams from the crude unit (Figures 4-3 and 4-4); fluid catalytic cracking units; hydrocracking units; gasoline treating units; and pumps, flanges, and other sources of fugitive emissions; and (2) nonprocess emissions from wastewater treatment facilities, heaters and boilers, and facilities for storage and handling of benzene and gasoline.

Benzene is recovered from the reformate of catalytic reforming units. For benzene production, toluene dealkylation processes are used to convert higher aromatics in reformate-mixed aromatics to benzene. The average distribution of aromatics in reformate is 2 to 4 percent benzene,

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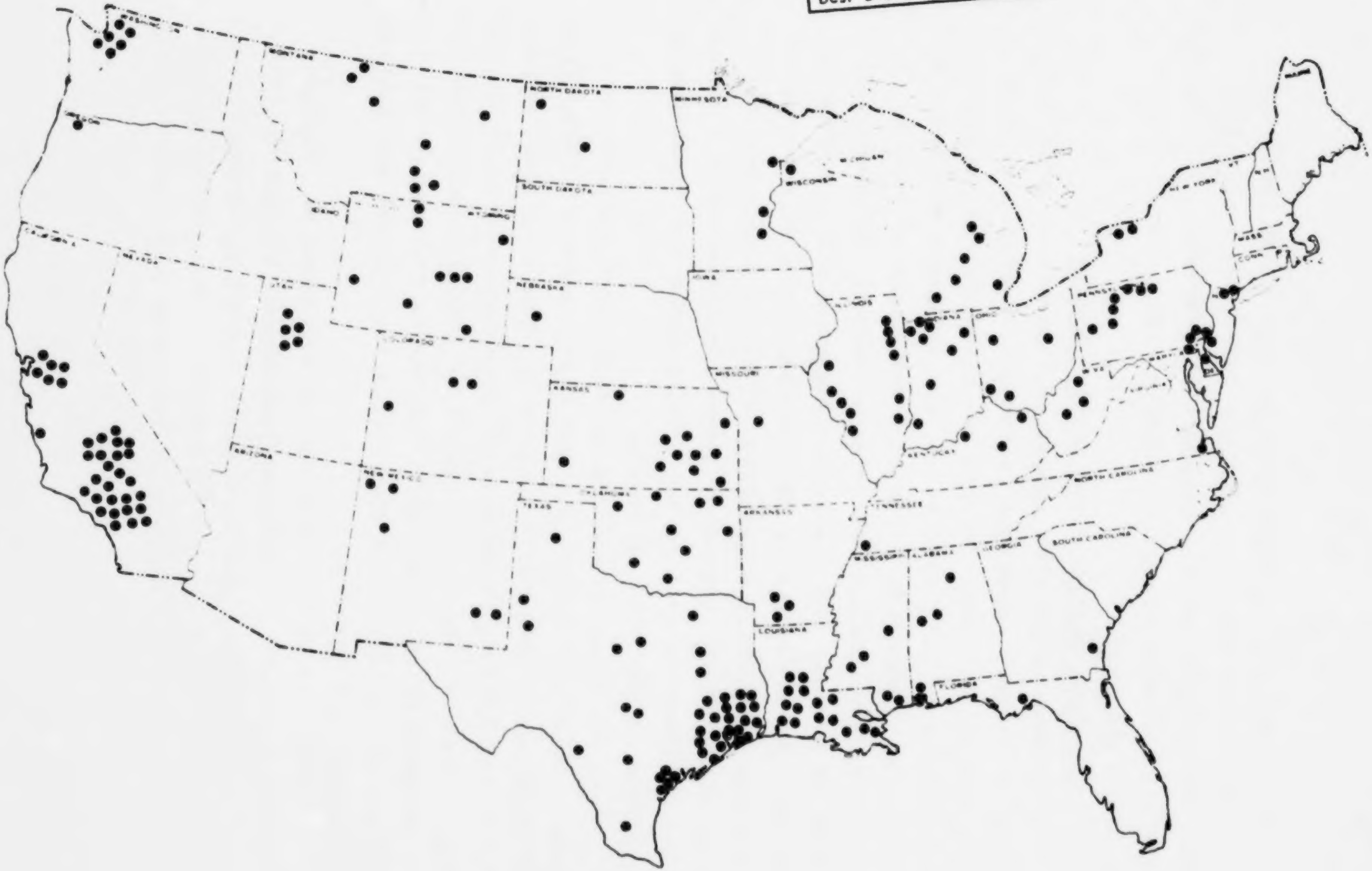
WASHINGTON
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NEVADA
IDAHO
MONTANA
WYOMING
UTAH
COLORADO
ARIZONA
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
MICHIGAN
ILLINOIS
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
PENNA
NEW YORK
MASS
CONN
MAINE

Figure 4-1. Location of United States oil refineries (not including Alaska, Hawaii, Puerto Rico, and asphalt or very small plants).

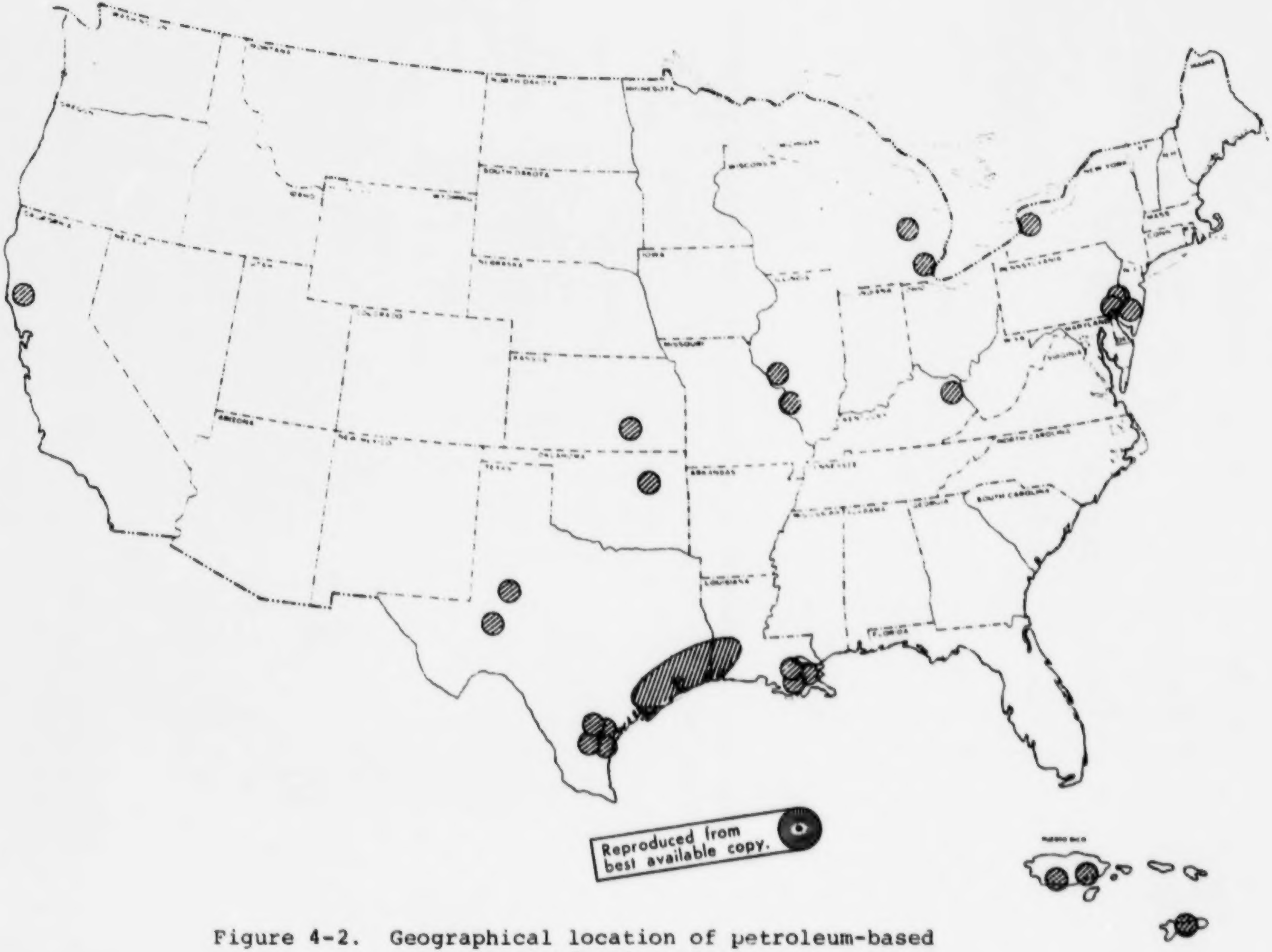

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Figure 4-2. Geographical location of petroleum-based benzene production plants.

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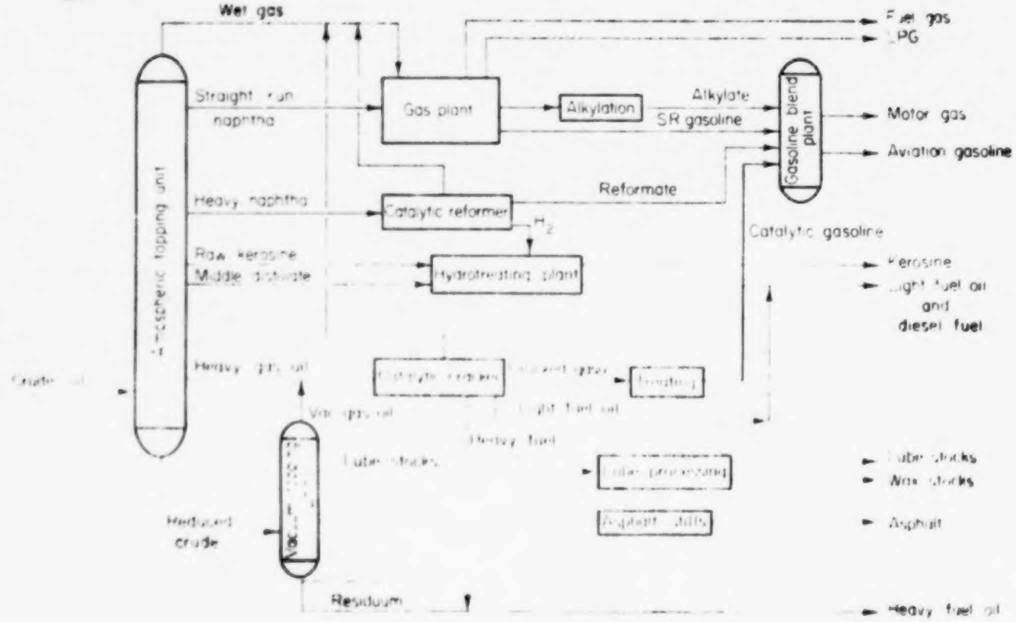
Wet gas
Fuel gas
LPG
Straight run naphtha
Gas plant
Alkylation
Alkylate
SR gasoline
Gasoline blend plant
Motor gas
Aviation gasoline
Atmospheric topping unit
Heavy naphtha
Catalytic reformer
Reformate
$H_2$
Catalytic gasoline
Raw kerosine
Middle distillate
Hydrotreating plant
Kerosine
Light fuel oil and diesel fuel
Crude oil
Heavy gas oil
Catalytic cracker
Treating
Vac gas oil
Light fuel oil
Heavy fuel
Lube stocks
Lube processing
Lube stocks
Wax stocks
Reduced crude
Vac
Asphalt stills
Asphalt
Residuum
Heavy fuel oil

Figure 4-3. Processing plan for typical intermediate refinery. Source: Ref. 130.

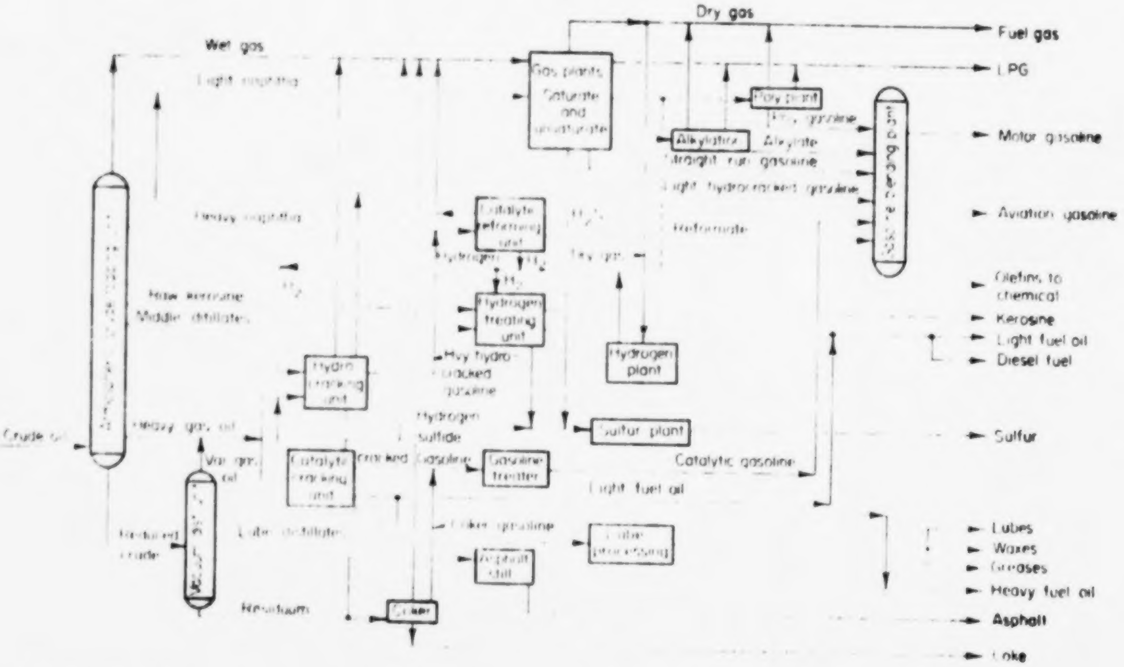
Dry gas
Fuel gas
Wet gas
LPG
Light naphtha
Gas plants
Saturate and unsaturate
Poly plant
Poly gasoline
Alkylation
Alkylate
Straight run gasoline
Light hydrocracked gasoline
Gasoline blending plant
Motor gasoline
Aviation gasoline
Heavy naphtha
Catalytic reforming unit
Reformate
Hydrogen
$H_2$
Dry gas
Olefins to chemical
Raw kerosine
Middle distillates
Hydrogen treating unit
Kerosine
Light fuel oil
Diesel fuel
Hydro cracking unit
Hvy hydro cracked gasoline
Hydrogen plant
Crude oil
Heavy gas oil
Hydrogen sulfide
Sulfur plant
Sulfur
Vac gas oil
Catalytic cracking unit
Cracked gasoline
Gasoline treater
Catalytic gasoline
Light fuel oil
Reduced crude
Lube distillate
Coker gasoline
Lube processing
Lubes
Waxes
Greases
Asphalt still
Heavy fuel oil
Residuum
Coker
Asphalt
Coke

Figure 4-4. Processing plan for typical complete refinery. Source: Ref. 130.

15 to 19 percent toluene, 28 to 30 percent xylene, and the remainder other aromatics.[107] In the reforming-separation process, a petroleum fraction is catalytically reformed; benzene and other aromatic hydrocarbons removed from the reformate by solvent extraction then are distilled fractionally to separate the solvent. Benzene originally present in the petroleum fraction goes through the process essentially unchanged. The total benzene yield includes both this unchanged benzene and benzene from various precursors, primarily cyclohexane and methylcyclopentane.[43]

Benzene is also produced by dealkylation of toluene or toluene-containing stocks such as heavy catalytic reformates, catalytic cycle oils, and the like. Several processes, both catalytic and thermal, are utilized. Dealkylation is performed in the presence of hydrogen (often catalytic-reformer hydrogen), and no solvent extraction of the product is necessary.[59,81] This process is commonly practiced in a petrochemical complex rather than in a petroleum refinery.

Whether benzene is produced as a refinery product or mixed in the gasoline pool may not significantly affect atmospheric concentrations, since the same quantity of benzene is being handled (unless toluene dealkylation is performed). Although separation of benzene probably creates more fugitive emissions, all refineries emit benzene but in ill-defined quantities.

The only available data on benzene exposures concern occupational exposures and indicate a common 8-hour time-weighted-average (TWA) exposure of 1 to 5 ppm.[41] Young et al. also report benzene concentrations at various refineries.[163] The highest concentrations were measured near pumps (1 to 16 ppm) and near a benzene tower reboiler (<1 to 6 ppm).

Refineries contain numerous tanks for blending gasoline and storing components; evaporation from these tanks probably is a major source of benzene emissions. Emission estimates for storage tanks are presented in storage and transport emissions (Section 4.2.4).

No data are available on benzene emissions from refineries, nor have estimates been published. Since process emissions appear to occur from leaks, only an order-of-magnitude estimate can be made. Refinery emission factors for hydrocarbons from revised EPA AP-42 data are used in these estimates.[117] In emissions from cooling towers, valves and flanges, relief valves, pump seals, sampling and other miscellaneous losses, we estimate 1 percent of the hydrocarbons is benzene. In hydrocarbon emissions from blowdowns, process drains, and vacuum jets, we estimate 0.1 percent is benzene. Benzene emission factors used for cooling towers are 10 percent of revised AP-42 levels, based upon data provided by Shell Oil.[44] Benzene emissions from catalytic cracker regenerators are assumed to be very low because a combustion temperature of approximately 1200°F and an atmosphere of excess oxygen, as used in these operations, are not conducive to benzene formation.

The emission factors used from AP-42 estimate emissions from controlled and uncontrolled sources.[117] Although all refineries have some control, it assumed that refineries with less than 35,000 barrels per stream day (BPSD) are uncontrolled. In 1973, this segment of the industry represented 19.6 percent of total U.S. crude capacity.[76] Because most subsequent capacity increases have been in larger refineries, the portion of uncontrolled capacity is reduced to 15 percent for these estimates. The overall emission factors, expressed as pounds of benzene emitted per 1000 bbl of crude feed, are 0.415 for controlled refineries, 2.27 for uncontrolled refineries, and a weighted estimate of 0.759 for the industry average.

The estimated total U.S. annual benzene emissions from refineries = $(15.4 \times 10^6)^*$ $(350)^+$ $(0.759 \times 10^{-3})$

= 2.1 Gg/yr (4.1 million lb/yr).

Estimated benzene emissions from a 150,000 BPSD "controlled" refinery are 21,800 lb/yr; estimated emissions from a 10,000 BPSD "uncontrolled" refinery are 7900 lb/yr.

Estimates of benzene emissions from benzene production plants are based on a Union Carbide emission factor of 0.035 lb per ton of benzene produced.[130] Because this factor is based on an aromatics plant utilizing a crude olefins by-product stream, it is not necessarily representative of all benzene production operations.

The total U.S. annual benzene production emissions based on this emission factor

= $(1.45 \times 10^9)^§$ $(7.365^{**}/2000)$ $(0.035)$

= 0.08 Gg/yr (0.19 million lb/yr).

### 4.2.2 Coke Ovens and Coke Oven By-Production

Although coke ovens represent a relatively minor benzene production source (about 5 to 8 percent of U.S. total), they are a potentially significant local environmental benzene source because of their poor vapor containment. Appendix C-1 lists the coal-derived benzene producers in the United States, their locations, and their production capacities.[28] Figure 4-5 depicts the geographic distribution of these facilities.

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[*] U.S. refinery crude feed rate, $15.4 \times 10^6$ barrels/day.[115]

[+] Days operation/year.

[§] U.S. benzene production, $1.49 \times 10^9$ gallons/year.[5]

[**] Conversion for benzene lb/gallon.

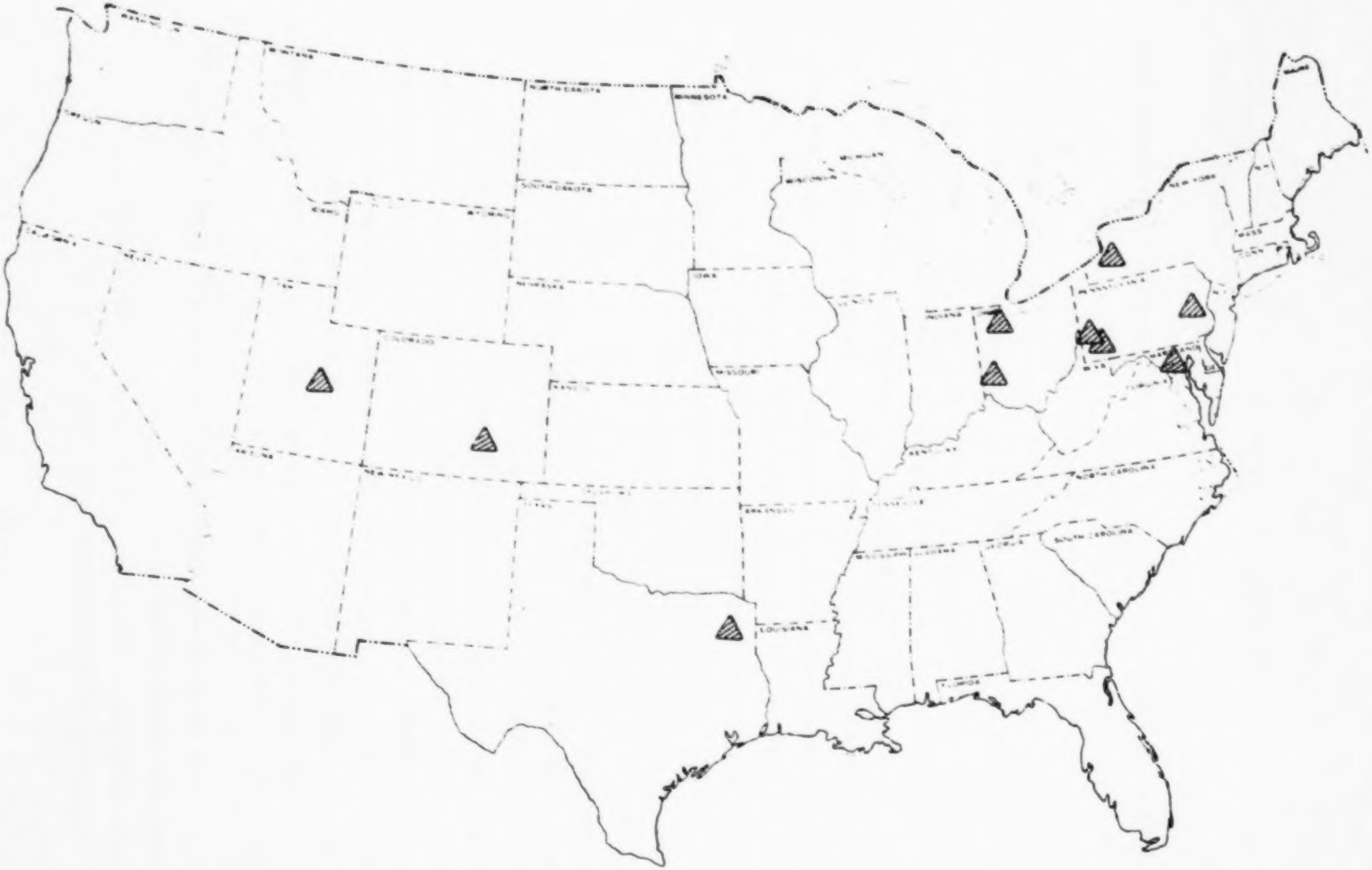

NORTH DAKOTA
MINNESOTA
SOUTH DAKOTA
NEBRASKA
IOWA
COLORADO
KANSAS
MISSOURI
INDIANA
KENTUCKY
ARKANSAS
LOUISIANA
FLORIDA
NEW YORK
PENNSYLVANIA
NORTH CAROLINA
SOUTH CAROLINA

Figure 4-5. Geographical location of coal-derived benzene production plants.

Major aromatic hydrocarbon constituents of coke-oven gas generated during coking operations are about 0.66 percent by volume benzene, 0.13 percent toluene, 0.05 percent xylene, and less than 0.10 percent other aromatics.[59] Higher temperatures produce greater amounts of aromatic hydrocarbons, particularly benzene, and lesser quantities of paraffinic, napthenic (saturated alicyclic), and unsaturated hydrocarbons.[59,153] The yield of light oil from coke ovens producing blast-furnace coke ranges from 13 to 17 $Mm^3/Mg$ (3 to 4 gallons per ton) of coal carbonized.[81] The principal constituents of this oil are benzene (60 to 85 percent), toluene (6 to 17 percent), xylene (1 to 7 percent), and solvent naphtha (0.5 to 3 percent).[153] Light oil is recovered by the following methods:[81,153]

- Compression and cooling at pressures of 1.0 MPa (10 atmospheres) and temperatures below -70°C.
- Adsorption on solids such as activated carbon (or silica gel) and recovery from the carbon by direct or indirect steam heat.
- Continuous countercurrent absorption by solvents, e.g., petroleum wash oil, a coal-tar fraction, or other absorbent, followed by steam distillation stripping to recover the light oil.

This crude light oil is then fractionated to produce benzene, toluene, and xylene. A typical amount of benzene recovered from coke-oven gas is 7.7 $Mm^3/Mg$ (1.85 gallons per ton) of coal input.[34]

Distillation of coal tar is another source of benzene. The composition of coal tar, although chiefly determined by the coking and recovery processes, also varies with the grade of raw coal. Coke-oven by-production generates 33 to 50 $Mm^3$ per Mg (8 to 12 gallons per ton) of tar according to the grade of coal coked. This tar is fractionally distilled to yield light, middle, heavy, and anthracene oils. The light oil fraction (approximately 5 percent of the tar) is generally added to the major portion of light oil recovered from coal gas to be refined for its benzene content.

Figure 4-6 illustrates the basic coke-oven operation and major points of air pollutant emissions.[83] Emissions occur from various points during charging, pushing, and quenching operations; from doors during the coking cycle; and from the waste-gas stack.

An uncontrolled charging operation is believed to have the greatest potential for emissions of hydrocarbons, and thus of benzene. When the moist coal comes into contact with the hot oven floor and chamber walls, evaporation and coking (distillation and cracking of volatile components) start immediately. If not controlled, the liberated vapors and gases escape to the open air.[116] These emissions may vary widely depending on the characteristics of the coal and operating practices. Hydrocarbon emissions from charging have been reported to range from 57 to 800 grams per ton of coal charged at some European coke plants.[14] Total emissions of about 5.4 Mg (6 tons) per day [including 0.15 Mg (0.4 ton) of benzene-containing hydrocarbons] are generated from a battery of 65 high-capacity 6 m (19.7 ft) ovens.[25]

Topside emissions of fugitive benzene occur from a variety of sources including leakage from weakened refractory materials, ascension-pipe-elbow covers, leveling apertures, badly fitted charging-hole covers, and collecting main pipe valves.

Coke pushing involves the discharge of incandescent coke from an oven on the coke side by operation of a ram on a pusher machine on the push side. This operation is believed

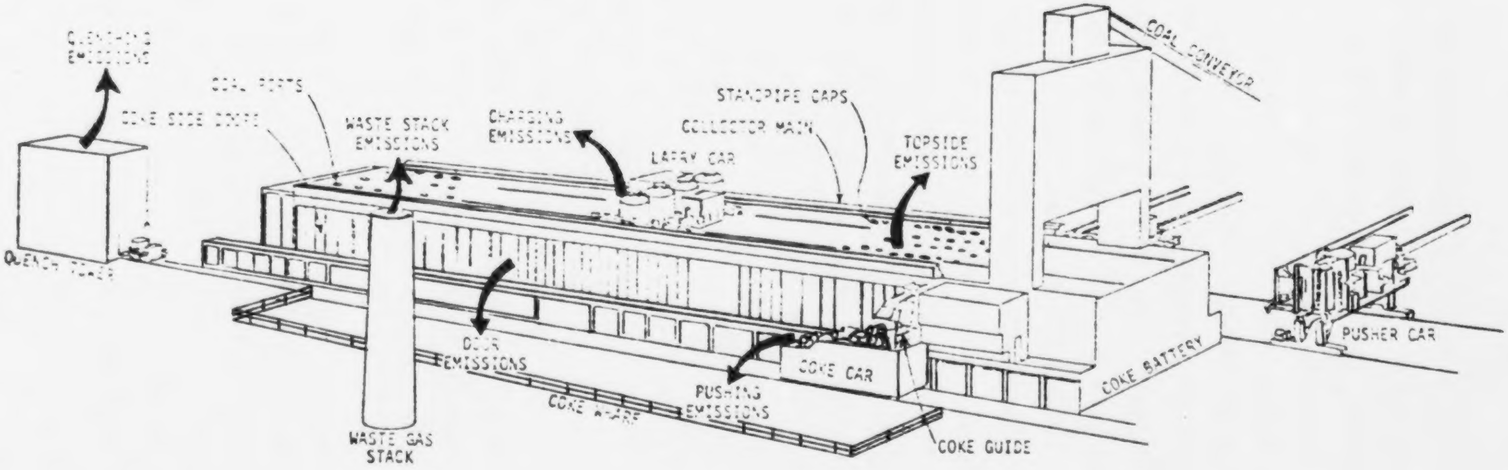

QUENCHING EMISSIONS
COAL PORTS
COKE SIDE DOORS
WASTE STACK EMISSIONS
CHARGING EMISSIONS
LARRY CAR
STANDPIPE CAPS
COLLECTOR MAIN
TOPSIDE EMISSIONS
COAL CONVEYOR
QUENCH TOWER
DOOR EMISSIONS
COKE WHARF
WASTE GAS STACK
PUSHING EMISSIONS
COKE CAR
COKE GUIDE
COKE BATTERY
PUSHER CAR

Figure 4-6. Schematic diagram of by-product coke oven showing possible atmospheric emission sources for benzene.[83]

to be a major source of benzene emissions during the coking cycle.[136] Under optimum conditions, however, coal is completely carbonized, and coke pushing results in minimal benzene emissions because most of the aromatic compounds already have been drawn off to be recovered from the oven gas. Three tests performed to measure emissions during the pushing operation showed benzene levels in the range of 0.003 to 0.04 lb benzene per ton of coke produced.[145]

Door leaks represent one of the most significant emissions sources. A 1975 national survey assessing the compliance status of coke-oven facilities revealed that 57 percent did not comply with state air pollution regulations during the coking cycle because of door leaks on both push and coke sides of the ovens.[83] Leaks can be minimized by good maintenance of door seals or by using a special luting mixture to seal the oven before charging.

The combustion chamber gas (natural or cleaned coke-oven gas) used for firing leaves the battery after combustion and is emitted to the atmosphere via the waste-gas stack. Waste-gas stacks normally are in compliance with state regulations, even though they rarely are equipped with control devices. Thus, they are not likely to be important sources of atmospheric benzene in well-maintained operations.[83] Emissions can be significant, however, if coal or coke escapes through leaks into areas between the oven and the heating flue.

Quenching involves the flooding of pushed hot coke (1100+°C) with a huge quantity of water to cool it rapidly.[84] The large quantities of steam generated by this operation vary during the quench cycle. Emissions from quenching depend on the completeness of coking and the sources of quenching water. No data are available on benzene emissions from this operation.

The only available data on ambient benzene concentrations attributable to coking operations concern occupational exposures. Typical exposures to ambient benzene (in 8-hour, time-weighted averages) by occupation were measured within a coal-derived benzene recovery plant; these are listed in Table 4-8.

Table 4-8. EXPOSURES OF WORKERS TO BENZENE IN A COAL-DERIVED BENZENE PRODUCTION PLANT[49]

| Occupation | Benzene concentration (8-hour time-weighted average), ppm | Range, ppm |
|---|---|---|
| Agitator operator | 6.0 | 0.5 - 20 |
| Benzene loader and loader helper | 4.0 | 0.5 - 15 |
| Benzene still operator | 4.0 | 1 - 15 |
| Light oil still operator | 2.5 | 1 - 15 |
| Naphthalene operator | 10.0 | 2 - 30 |
| Analyst | 10.0 | 4 - 30 |
| Chemical observer | 10.0 | 4 - 50 |
| Foreman | 1.5 | 1 - 10 |

In Czechoslovakia, atmospheric benzene emissions generated in the coking and by-product recovery phases of benzene processing were assessed. Within coke-oven battery working areas, ambient benzene concentrations ranged from 50 $\mu g/m^3$ to 13.0 $mg/m^3$; in the recovery plant, the concentrations ranged from 50 $\mu g/m^3$ to an exceptional 145 $mg/m^3$, almost triple the limit imposed by Czechoslovakian standards (50 $mg/m^3$).[93] Within working areas of tar-processing plants, the analysis detected 0.3 $mg/m^3$ of emitted benzene.[93]

Our order-of-magnitude estimate of total annual benzene emissions from coking operations in the United States is based on a hydrocarbon emission factor of 6.9 lb emitted per ton of coal coked.[31] The benzene fraction of total hydrocarbon emission is based on coke-oven gas containing 34.8 percent hydrocarbons and 0.776 percent benzene. The value for hydrocarbon content is an average of two reported values, 36.1 and 33.6 percent.[119,111] The benzene concentration in coke-oven gas (0.776%) is the average of three plant measurements: 1.028 percent at a USSR plant, 0.686 percent at another USSR plant, and 0.615 percent at a West German plant.[77,82,85]

Annual U.S. benzene emission from coking operations

$= (50.4 \times 10^{6})^{*}(6.9)^{+}(0.0223)^{\S}$

$= 3.52$ Gg/yr (7.76 million lb/yr).

The above calculation assumes that all hydrocarbons contain the same benzene fraction as those in coke-oven gas. This fraction probably depends on the time in the coking cycle and the source of the emission, and therefore is not a good index of benzene emissions from the by-product recovery process. It is applied because no specific data are available on emissions from by-product recovery.

Benzene emissions from a Czechoslovakian coke plant producing 4 million tons of coke per year are reported to be 1660 tons.[94] If a 75 percent by weight coal conversion to coke is assumed, this benzene emission rate of $4.15 \times 10^{-4}$ kg/kg coal charged leads to a U.S. benzene emission of 19.0 Gg/yr (41.8 million lb/yr). Thus the coking operations are

---

[*] Total annual U.S. coke-oven feed rate, tons of coal.[79]

[+] Hydrocarbon emission factor for coke ovens, lb/ton of coal.[31]

[§] Fraction of benzene in total hydrocarbons, utilizing level of 0.776 percent benzene in coke-oven gas and 34.8 percent hydrocarbons in coke-oven gas.[59]

potentially a major industrial source of benzene emissions.

In summary, data on benzene emissions from coke-oven and benzene-recovery plant operations are very meager, but pertinent occupational exposure levels have been measured. A study on by-product plants being conducted by Research Triangle Institute may improve the accuracy of the estimates. Data on by-product recovery plants indicate that exposures vary with occupation and over extended periods of time. Charging of coal is regarded as the greatest potential source of benzene emission in coke-oven operations; however, leakage from doors may be an equally or more serious source in U.S. plants. Lesser quantities are attributed to topside leakage, pushing, quenching, and waste-stack emissions.

### 4.2.3 Benzene Consumption

This subsection addresses benzene emissions from the major commercial uses of benzene. Total 1976 U.S. consumption of benzene in such uses was 5.3 to 5.6 $Mm^3$ (1.4 to 1.5 billion gallons).[5] Primary usage is for the manufacture of such chemicals as nitrobenzene, ethylbenzene, maleic anhydride, cumene, phenol, chlorobenzenes, cyclohexane, and detergent alkylate, as well as other nonfuel products and solvents, as shown in Figure 4-7. The production capacities for the major compounds are presented in Table 4.9. Producers of various compounds (excluding solvents) are listed in Appendix D-1, with their locations and 1976 capacities. Figure 4-8 shows the geographic distribution of these facilities. Primary locations are along in the Gulf coast, in the northeastern section of the United States, and in Puerto Rico.

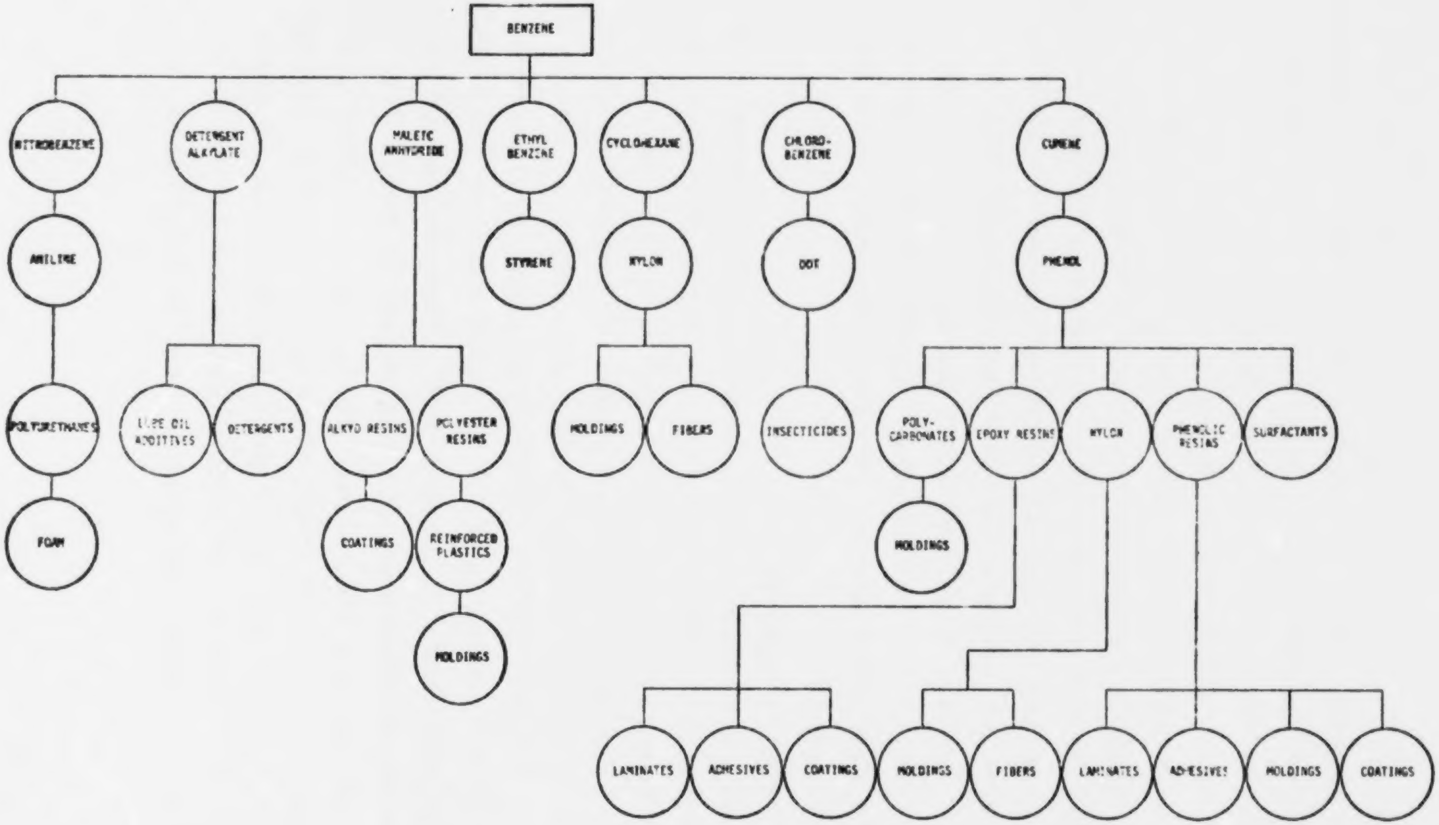

BENZENE
NITROBENZENE
ANILINE
POLYURETHANES
FOAM
DETERGENT ALKYLATE
LUBE OIL ADDITIVES
DETERGENTS
MALEIC ANHYDRIDE
ALKYD RESINS
COATINGS
POLYESTER RESINS
REINFORCED PLASTICS
MOLDINGS
ETHYL BENZENE
STYRENE
CYCLOHEXANE
NYLON
MOLDINGS
FIBERS
CHLORO-BENZENE
DDT
INSECTICIDES
CUMENE
PHENOL
POLY-CARBONATES
MOLDINGS
EPOXY RESINS
NYLON
PHENOLIC RESINS
SURFACTANTS
LAMINATES
ADHESIVES
COATINGS
MOLDINGS
FIBERS
LAMINATES
ADHESIVES
MOLDINGS
COATINGS

Figure 4-7. Flow chart for benzene derivatives and their uses.

Source: Ref. 66.

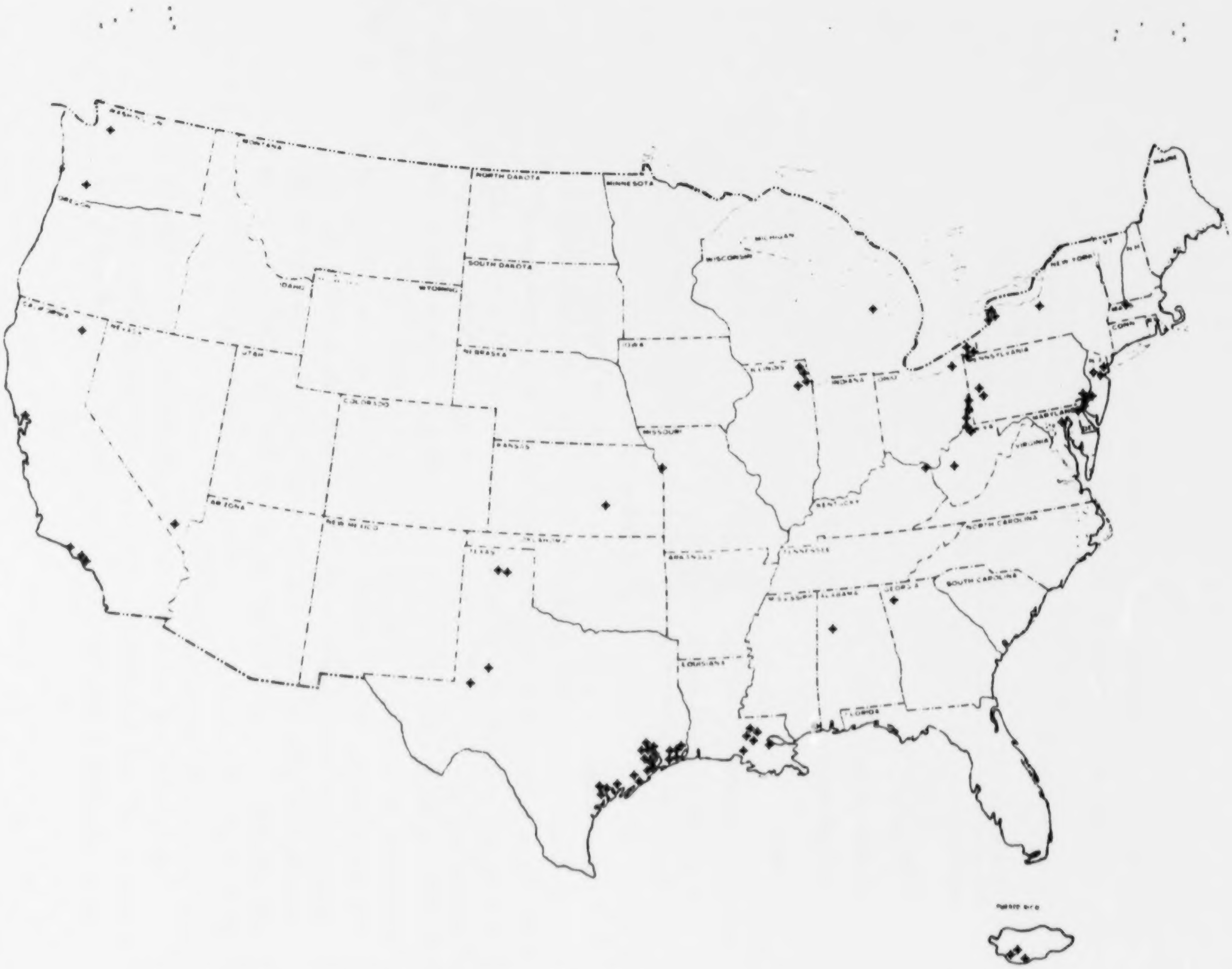

WASHINGTON
MONTANA
NORTH DAKOTA
MINNESOTA
MICHIGAN
WISCONSIN
MAINE
VT
N H
NEW YORK
OREGON
IDAHO
WYOMING
SOUTH DAKOTA
CALIFORNIA
NEVADA
UTAH
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
PENNSYLVANIA
CONN
COLORADO
KANSAS
MISSOURI
MARYLAND
VIRGINIA
KENTUCKY
ARIZONA
NEW MEXICO
OKLAHOMA
ARKANSAS
TENNESSEE
NORTH CAROLINA
TEXAS
MISSISSIPPI
ALABAMA
GEORGIA
SOUTH CAROLINA
LOUISIANA
FLORIDA
PUERTO RICO

Figure 4-8. Geographical location of benzene-consumption plants.

Table 4-9. ANNUAL (1976) PRODUCTION CAPACITY FOR SOME MAJOR CHEMICAL COMPOUNDS IN WHICH BENZENE IS USED AS AN INTERMEDIATE

| Chemical | 1976 Production[28] | |
|---|---|---|
| | Gg/yr | $10^6$ lb/yr |
| Nitrobenzene | 480 | 1065 |
| Ethylbenzene | 3890 | 8566 |
| Maleic anhydride | 188 | 415 |
| Cyclohexane | 1230 | 2706 |
| Cumene | 1720 | 3785 |
| Chlorobenzene (mono) | 313 | 690 |
| Detergent alkylate | 392 | 865 |

## Nitrobenzene

Nitrobenzene ($C_6H_5NO_2$) is prepared by direct nitration of benzene, using mixed nitric and sulfuric acids (see Appendix Figure D-1) in both batch and continuous operations. A typical batch reaction vessel (or nitrator) is sized for 450 to 700 kg (1000 to 1500 lb) of benzene and operates on a time cycle of 2 to 4 hours. The nitrobenzene produced in this reaction is principally used directly in the manufacture of aniline. Newer plants use the continuous process, which is fundamentally the same as the batch process except for smaller reaction units, lower nitric acid concentrations, and higher reaction rates. Overall, it is estimated that some 85 percent of the chemical is used in the manufacture of aniline.[59]

Reactors and acid concentration systems are the main sources of any atmospheric emissions during processing. These emissions are vented to absorbers, where any $NO_x$ is oxidized with air and absorbed in water to produce recycled nitric acid.

Monsanto Research Corporation reports that ambient benzene emissions from nitrobenzene production in 1975 totaled 3.39 Gg (7.47 million lb).[97] On the basis of a total 1975 domestic nitrobenzene production capacity of 480 Gg (532,500 ton), the resulting benzene emission factor is 0.007 kg per kg of product.[81]

## Aniline

Aniline ($C_6H_5NH_2$) is produced either by chemical reduction or catalytic hydrogenation of nitrobenzene. The traditional batch method (now seldom used) involves reduction with iron filings and hydrochloric acid. Most modern plants practice continuous catalytic vapor-phase hydrogenation because it is more economical.[59,66]

No data are available on atmospheric benzene emissions from the manufacture of aniline. Because benzene is present principally as an impurity in nitrobenzene, this does not appear to be an important benzene emission source.

## Ethylbenzene/Styrene

Ethylbenzene ($C_6H_5C_2H_5$) is prepared primarily by the liquid-phase Friedel-Crafts alkylation of benzene with ethylene. Styrene ($C_6H_5CHCH_2$) is produced solely by the catalytic dehydrogenation of ethylbenzene.

In the production of ethylbenzene, aluminum chloride is the catalyst and ethyl chloride or hydrogen chloride is the promoter. The process takes place within a brick-lined steel tower or a glass-lined reactor operating at 90 to 100°C and at atmospheric pressure. Liquid products from the alkylator are cooled, then passed through a settler, where the aluminum chloride complex is removed and returned to the alkylator (Appendix Figure D-2). The water-washed alkylate is scrubbed with 20 percent caustic for neutralization, then separated into components in a series of distillation columns, the first of which removes the benzene for recycle to the reactor. The gaseous products leaving the top of the alkylator, (unreacted ethylene, some benzene, hydrogen chloride, and inerts) enter a condenser, from which the recovered benzene flows back to the alkylator. The off-gas is scrubbed for final benzene recovery, with recycled polyethyl benzenes as absorbents; the gas is then water-washed for HCl removal before being vented or compressed for use as fuel.[81,59,106]

Other major ethylbenzene production processes using a benzene feed are the Alkar process and the Mobil/Badger ethylbenzene process. The Alkar process utilizes a fixed-bed catalyst and can handle a mixed olefins feed to produce high-purity ethylbenzene.[106] The reactor effluent is cooled and flashed to remove noncondensibles when required, i.e. when mixed olefins contain saturated hydrocarbons. The Mobil/Badger ethylbenzene process flow is similar. In both processes the uncondensed reactor effluent vapor can be vented to the process fuel gas system.[106]

Recovery of ethylbenzene from mixed xylenes is the only other significant source of ethylbenzene capacity; it accounts for approximately 6 percent of domestic production.[47] This process produces no benzene emissions.

Direct dehydrogenation of ethylbenzene is the only commercial process currently employed for the manufacture of styrene. Preheated ethylbenzene and superheated steam are fed into a reactor containing a selective dehydrogenation catalyst. Available production routes involve either an adiabatic or an isothermal reactor. Steam serves as a heat source and a diluent to improve conversion. The reactor effluent is cooled and flashed, the noncondensibles going to fuel and liquid going to a distillation train.[106,68]

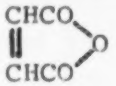
A case study (with unspecified monitoring methodology) of an ethylbenzene plant of 101 Gg/yr (223 million lb/yr) capacity reported a scrubber vapor effluent containing 11 kg of benzene per Mg of product (22 lb per ton of product).[66] If uncontrolled effluent were vented into the atmosphere, annual emissions would be 1.1 Gg (1226.5 tons) of benzene. Ethylbenzene production using a benzene feed process can be calculated as the total domestic production of 2.14 Tg (2.36 million tons)[5] minus the ethylbenzene production from mixed aromatics (0.190 Tg, 0.209 million tons), or 1.95 Tg (2.15 million tons). Application of this emission factor yields a hypothetical uncontrolled annual emission of 21.46 Gg (47.3 million lb) of benzene. This emission rate is reported to be representative of older technology, resulting in an emissions value that is much higher than the present industry wide total.[37] The controlled benzene emission from a combined ethylbenzene/styrene facility reported by Union Carbide[37] is $0.065 \times 10^{-5}$ kg/kg of product. Application of this emission factor gives total benzene emissions of 0.14 Gg/yr (0.308 million lb/yr). It not known what percentage of domestic producers apply emission controls comparable to those at the facility described.

The national emission inventory for styrene production plants reported by Houdry[68] indicates that benzene emissions range between $2 \times 10^{-6}$ and $2.2 \times 10^{-3}$ kg/kg of styrene, based on data from 1.40 million tons of the total 1975 production of 2.2 million ton styrene.[5] Using an average emission factor of $1.5 \times 10^{-3}$ kg/kg, PEDCo's estimates of total benzene emissions is 2.9 Gg/yr (6.48 million lb/yr). Major emission sources are the distillation column hotwell vents.[68]

The Houdry data for styrene plants show higher emission rates than Union Carbide data for ethylbenzene plus styrene trains.[68] To estimate the ethylbenzene process emissions, it is assumed that reactor effluent vents are controlled and that fractionation vacuum jet vents represent the major emission sources. Houdry reports that the total hydrocarbon losses from distillation vents at styrene plants are 0.00062 ton/ton of styrene.[68] This emission factor is used in estimating benzene emissions from ethylbenzene processes because benzene is the major volatile hydrocarbon present in the fractionation train of these processes. In ethylbenzene production a benzene feed of 1.95 Tg (2.15 x $10^6$ tons) yields an estimated annual emission rate of 1.2 Gg (2.67 million lb).

In summary, benzene emission estimates are
1.2 Gg/yr (2.67 million lb/yr) - for ethylbenzene production
2.9 Gg/yr (6.48 million lb/yr) - for styrene production.

## Maleic anhydride

Maleic anhydride  $\left.\begin{matrix}\text{CHCO}\\ \| \\ \text{CHCO}\end{matrix}\right\rangle O$ is produced from the oxidation of benzene in the presence of a suitable catalyst (see Appendix Figure D-3). Standard commercial practice is to conduct the reaction in the vapor phase utilizing a $V_2O_5$-based catalyst. Benzene is mixed with an excess of preheated air before being admitted to a multitubular catalytic reactor. Effluent vapors, consisting of maleic anhydride (MAN), maleic acid, carbon oxides, water, and benzene, are cooled and passed through a partial condenser and separator, where the bulk of the maleic anhydride is separated from the noncondensibles. The overhead material from the separator still contains some maleic anhydride; this material is recovered as maleic acid through absorption in aqueous (or nonaqueous) solvents. The crude maleic acid is converted to the anhydride and distilled to meet purity specifications.

Maleic anhydride is also obtained through vapor-phase oxidation of butenes and as a by-product of phthalic anyhydride.[105] However, these techniques are used less frequently than the method described above.

Two percent of the U.S. MAN capacity of 485 million lb/yr is derived from phthalic anhydride by-production and 16.7 percent from butenes.[55] Thus, for purposes of calculating benzene emissions, MAN output from these processes is deducted and only the benzene-derived MAN production (81.3 percent) is considered.

The most significant process source of benzene emissions is the product-recovery condenser vent. Scrubbers are usually equipped to recover uncondensed maleic anhydride before venting effluent gases to the atmosphere. Data from stack tests at one MAN plant indicate benzene emissions from the off-gas (with an inoperative incinerator): the total hydrocarbon level was measured at 1150 ppm (as methane equivalents), with 180 ppm of benzene.[45] A 1972 emissions inventory of seven other MAN plants, some of which are known to be equipped with large scrubber units, shows controlled benzene emissions ranging from 0.06 to 0.20 kg of benzene per kg of maleic anhydride produced. Monsanto Research reported total benzene emissions from all plants to be 15.8 Gg/year (34.8 million lb/year).[88] The reported emission factor for a plant with a product scrubber is 0.0967 kg per kg of product.[88]

Because of these high rates of emission of benzene and other pollutants, maleic anhydride production is the largest stationary source of benzene emissions.

### Cyclohexane

Cyclohexane ($C_6H_{12}$) is manufactured commercially by hydrogenation of benzene and by distillation from petroleum. Of 803 Gg (1.7 billion lb) produced domestically in 1975, approximately 75 percent was produced by catalytic hydrogenation of benzene.[5,66] This process is carried out in the liquid phase by contacting benzene, hydrogen, and recycled cyclohexane over a platinum catalyst. The yield of cyclohexane is approximately 95 percent.[20,66] Although off-gases may contain benzene, they are rich enough to be sent to the fuel gas system.[66,106] Thus, benzene emissions probably are mainly fugitive. Because of its relative simplicity, this process appears to be a minor source of benzene emissions.

### Cumene

Cumene [$C_6H_5CH(CH_3)_2$], a naturally occurring compound present in many petroleum crudes, is manufactured synthetically by liquid- or vapor-phase alkylation of benzene with propylene. It is used predominantly for synthesis of phenol and acetone. Solid phosphoric acid (SPA) and aluminum chloride are used in the most common processes for commercial production of cumene. The SPA process requires a reactor and three distillation columns, one each for rejection of propane, recycle of unreacted benzene, and rerunning the cumene product to reject a minor quantity of polyalkylated materials (see Appendix Figure D-4). The aluminum chloride process is similar, but requires additional equipment to dry recycled streams and neutralize reaction products.

Domestic production of cumene in 1975 totalled 893 Gg (1.97 billion lb).[5] Union carbide reports a benzene emission factor of $2.45 \times 10^{-4}$ kg/kg of cumene produced. Factoring this value with 1975 cumene production data yields a total estimated annual benzene emission rate of 0.22 Gg/yr (0.48 million lb/yr).

## Phenol

Phenol ($C_6H_5OH$) can be manufactured synthetically by benzene sulfonation, chlorobenzene and toluene oxidation, cumene peroxidation, and the regenerative Raschig process. Domestic phenol production in 1975 was 780 Gg (1.72 billion lb).[5] Synthetic processes have long accounted for nearly all U.S. production. Because the cumene method accounts for over 90 percent of total U.S. phenol capacity,[81] this is the only mechanism described. This process essentially involves only two steps (see Appendix Figure D-5). First, air is introduced into a vigorously stirred emulsion of slightly alkaline, aqueous sodium carbonate with purified cumene to produce cumene hydroperoxide.[105] Then diluted sulfuric acid is added to effect cleavage of the compound directly into phenol and acetone.

Atmospheric emission of "spent air" containing benzene exhausted from the oxidizer is the largest single source of emission from cumene-process phenol plants.[105] Normally, effective multiple-stage refrigeration condensation systems and other equipment (such as scrubbers, activated carbon absorbers, or incinerators) are used for recovery and recycle of unconverted cumene (and benzene). One respondent to a phenol plant survey reported stack test data showing a controlled emission of $1.5 \times 10^3$ kg benzene per kg of product phenol from an oxidation unit at a plant with an average production of 113 Gg (0.25 billion lb) per year.[105]

This plant relies on refrigeration condensation equipment primarily to remove cumene from the oxidizer off-gas and only secondarily to control emissions. Another plant in this survey reported a benzene emission rate of 2 x $10^{-6}$ kg/kg of phenol from the postoxidizer concentration condensor vent.[105] A new phenol plant under construction shows no benzene point-source emissions.[44] Also, Union Carbide reports that the reported benzene emission rate of 1.5 x $10^{-3}$ kg/kg is one or two orders of magnitude higher than the controlled emission levels it achieves.[37]

Uncontrolled benzene emissions from plants utilizing toluene oxidation and benzene sulfonation are estimated to be 1.2 x $10^{-3}$ kg/kg and 1.2 x $10^{-4}$ kg/kg of phenol, respectively.[66]

In estimation of annual benzene emissions from phenol plants, it is assumed that half of the production capacity is from controlled operations and that control efficiency is 95 percent. Based on phenol production of 2.2 billion pounds in 1976 and the following production breakdown by process, the estimated benzene emissions are as follows:

| Process | Portion of total capacity[55] % | Phenol production, $10^6$ lb/yr | Emission factor uncontrolled, ton/ton | Emission rate, $10^6$ lb/yr |
|---|---|---|---|---|
| Cumene peroxidation | 89.2 | 1962 | 0.0015 | 1.62 |
| Toluene oxidation | 5.2 | 114 | 0.0012 | 0.08 |
| Benzene sulfonation | 5.6 | 123 | 0.00012 | 0.01 |
| Total 0.77 Gg/yr (1.71 million lb/yr) | | | | |

## Chlorobenzenes

Chlorobenzenes ($C_6C_{6-x}Cl_x$) are manufactured by batch or continuous processes (Appendix Figure D-6). In the batch method, chlorine is bubbled through dry benzene contained in a cast-iron or steel tank (chlorinator), with iron turnings as catalyst. The solution is then neutralized with aqueous (10%) caustic soda and separated into several fractions by distillation, the bulk of which (75%) is pure chlorobenzene. Residue from the distillation is the principal source of para- and orthodichlorobenzenes. Hydrogen chloride formed in the chlorinator is scrubbed with benzene or chlorobenzene to remove organic spray and is absorbed in water to give hydrochloric acid. Neutralization causes the settling out of a sludge rich in dichlorobenzenes. This sludge is further processed to recover the para- and orthodichlorobenzene isomers.

Continuous processing involves a combination of chlorination and fractionation, wherein the monochlorobenzene is isolated as quickly as it is formed. Monochlorobenzene withdrawn from the fractionating column is neutralized and distilled in the same manner as in the batch process.[59] The manufacture of paradichlorobenzene, the primary product, is accomplished by chlorinating benzene in the presence of aluminum chloride. An alternative process for production of monochlorobenzene is a catalytic vapor-phase oxychlorination of benzene with hydrogen chloride and air (Raschig process).

Presumably, the chlorination step is the principal source of atmospheric benzene emissions in processing of these chlorinated compounds. No quantitative emission data are given for specific production plants; however, Monsanto attributes total annual (1975) ambient benzene levels of 1065, 692, and 529 Mg (1170, 750, and 600 tons) to the manufacture of chlorobenzene, paradichlorobenzene, and orthodichlorobenzene, respectively.[97]

Based on the assumption that the average facility operates at 80 percent of capacity, emission factors are estimated as follows;

| Chemical | Annual capacity,[55] $10^6$ Kg | Emission, Gg | Benzene emission factor, kg/kg |
|---|---|---|---|
| Chlorobenzene | 303.9 | 1.065 | 0.0035 |
| Orthodichlorobenzene | 69.4 | 0.692 | 0.0100 |
| Paradichlorobenzene | 73.0 | 0.529 | 0.0072 |
| Total | 446.3 | 2.286 | 0.0051 |

### Detergent alkylate

Detergent alkylate (dodecylbenzene) is the name commonly given the product formed from the alkylation of benzene with dodecene. Any of three catalysts can be used: aluminum chloride, hydrogen fluoride, or sulfuric acid. The product, either branched or linear alkylbenzene (dodecylbenzene), depending on the olefin reactant, is separated from the catalyst, washed, and purified by distillation. Linear alkylbenzene is commonly made by alkylating benzene with a chlorinated n-paraffin at 38 to 66°C with aluminum chloride catalyst. Dodecylbenzene can be sulfonated into a surface-active agent.

Purifying the end product by distillation can cause emissions of airborne benzene from incineration of the light and heavy organic ends. No data are available on benzene emissions from production of branched alkylbenzene. The reported annual (1975) generation of benzene from linear alkylbenzene manufacture was 13.7 Mg (15 ton).[97] The emission rate for benzene from a controlled linear alkylate process was reported as $5 \times 10^{-4}$ kg/kg of product.[37] Based on an annual linear alkylbenzene production of 286 Gg (630 million lb), the annual benzene emission is estimated to be 144 Mg (0.32 million lb).[55] The latter emission rate is used in this inventory because it is based on the most recent emission data.

### Solvent operations

Although benzene has been used widely as an industrial solvent,[50] increasing awareness of its toxicity has caused users to replace it with other solvents for most applications.[40] Because of the relatively poor vapor containment in most solvent operations, solvent emissions for nonhalogenated solvents are essentially equal to solvent usage.[92] In 1966 the Council of Europe recommended that such materials as solvents, paints, and adhesives should not contain more than 5 percent benzene (unless enclosed and labeled), with eventual reduction to 1 percent.[16] In 1971 an International Labor Office (ILO) conference adopted a recommendation specifying a ceiling of 25 ppm for workplace exposure to benzene or products containing benzene at more than 1 percent by volume. It is reported that 0.5 percent would represent an extremely high estimate of the average benzene level in solvents.[38] The continual lowering of allowable levels of benzene to which workers may be exposed has caused benzene solvent users to reduce their consumption and/or institute emission controls.

Degreasing operations using benzene as a solvent are reported to have consumed as much as 73 Gg/yr (16.10 million lb/yr), with this amount ultimately being released to the atmosphere.[92] The degreasing operations covered in the reported figure are as follows:

| Operation | Benzene usage,[92] | |
|---|---|---|
| | Gg/yr | million lb/yr |
| Industrial degreasing | | |
| Metal furniture | 1.0 | 2.2 |
| Primary metals | 1.0 | 2.2 |
| Fabricated products | 1.0 | 2.2 |
| Other miscellaneous | 35.0 | 77.2 |
| Textile plants | 35.0 | 77.2 |
| Total | 73.0 | 161.0 |

Textile plants, the largest consumers of benzene as a solvent, use benzene for fabric scouring or cleaning. It is reported that the textile industry still uses benzene for this operation, even though it now uses many other solvents as well.[92,143]

Chevron reports that degreasers generally use either chlorinated hydrocarbons or higher-boiling solvents in which benzene would be present only as an impurity. Thus, they believe that the degreaser contributions to benzene emissions from solvent operations should be very much less than 10 percent.[38]

Finally, the re-refining of benzene-containing solvents is a potential source of benzene emissions. The typical solvent recovery system (Appendix Figure D-7) consists of a tank in which solids settle out, a pot still topped by a fractionating section, and a surface condenser to distill and liquify the vapor prior to collection in a holding tank. A salt such as sodium carbonate is then added to aid in separating water from the pure solvent. Although no quantitative data are reported, apparent sources of emissions include the settling tanks during filling and sludge drawoff, the still during drawoff of bottoms, the product receivers, and the water jet reservoir (if vacuum is produced by a barometric water jet). By creating a vacuum, the water jet entraps solvent vapors from the still.[50]

Other nonfuel uses

Other nonfuel uses of benzene that are regarded as potentially significant emission sources are listed below, with annual production rates and estimated atmospheric emissions:

| Chemical | Annual production,[55] $10^6$ lb/yr | Benzene emission[97] $10^3$ kg/yr | Benzene emission[97] $10^3$ lb/yr |
|---|---|---|---|
| Fumaric acid | 75 | 300.1 | 662 |
| Cumene sulfonate ammonium salt | N.A. | 1.6 | 3.5 |
| Cumene sulfonic acid | N.A. | 1.1 | 2.4 |
| Benzonitrile | N.A. | 0.3 | 0.7 |
| Anthraquinone | N.A. | N.A. | N.A. |
| Total emission | | ≈ 303 | ≈ 669 |

N.A. = Not available.

In summary, maleic anhydride appears to be the largest source of benzene emissions among the processes using benzene as an intermediate. The poor quality of the available data on benzene emissions from many of the processes, particularly solvent operations, makes it difficult to evaluate the environmental impacts of these processes.

Hydroscience Inc. is making detailed engineering studies of the following benzene consumption processes: ethyl benzene, maleic anhydride, nitrobenzene, cyclohexane, chlorobenzenes, and alkyl benzenes. Because these studies will include source testing and evaluation of best control technology, their results should greatly improve the reliability of the characterization of benzene emissions from these processes.

### 4.2.4 Storage and Transport Emissions

Storage and distribution of gasoline and benzene (including 'feedstock' benzene stored by noncaptive consumer industries) are potentially more significant sources of benzene emissions than benzene manufacturing processes. For the purposes of this report, it is assumed that little or no benzene is emitted in the storage and transport of consumer chemicals (ethylbenzene, cumene, cyclohexane, etc.) for which benzene is used as a feedstock in production. This assumption is justified by the normally low benzene concentrations in these chemicals.

4.2.4.1 Storage - Petroleum refinery bulk terminals and petrochemical plant storage facilities consist of closed-storage vessels, which include pressure, fixed-roof, floating-roof, and conservation tanks.

Pressure tanks are designed to withstand relatively high pressures and normally are used to store volatile fluids. They are never used for gasoline storage and seldom for benzene storage.

Ordinary fixed-roof tanks (vertical cylinders) normally are used to store low-volatility liquids. Many of the flat, conical, or domed roofs of these tanks have free vents open to the atmosphere; others have conservation vents that open at very slight positive pressures. (Appendix Figure E-1 shows a diagram of a typical fixed-roof storage tank.) Fixed-roof tanks are still used for gasoline storage, but state regulations require that these tanks be small.

Floating-roof tanks minimize vapor space and normally are used to store more volatile liquid fractions, such as gasoline and benzene, that emit vapors presenting potential fire or explosion hazards. These tanks are differentiated by type of floating-roof design: pan, pontoon, or double-deck. Pan-type tanks have a flat, metal plate roof. Extreme tilting or holes in the plate may cause it to buckle or sink, resulting in high losses of vapor. Other losses may occur from solar irradiation if the metal roof is in direct contact with the liquid surface. High liquid surface temperatures can cause hydrocarbons to boil and escape through the opening around the perimeter of the roof. The pan-type tank, placed in service more than 40 years ago, is seldom used in new construction. Pontoon-type tanks were designed to overcome the pan-roof hydrocarbon losses. Pontoon sections were added to the top of the exposed deck, with a drain placed in the center to solve any drainage problem. Ordinarily this roof is commonly used on tanks with very large diameters. In some pontoon-roof tanks a vapor trap is installed on the underside to retain vapors formed by the surface liquid boiling induced by solar heat. Double-deck floating roofs (Appendix Figure E-2) were introduced to reduce the effects of solar boiling and to provide rigidity. In this design, compartmented, dead-air space covers the entire liquid surface. The bottom deck of the roof is normally coned upward to trap any vapors entrained with incoming liquid or any vapors formed earlier in storage.

Conservation storage vessels include lifter-roof tanks and tanks with internal, flexible diaphragms or internal, plastic, floating blankets. Appendix Figure E-3 shows a diagram of a typical lifter-roof tank with variable vapor space. This type of vessel is similar to the fixed roof tank and is used for low-volatility liquids or low-pressure gaseous products. Fixed-roof tanks with plastic floating blankets are effective for controlling evaporation from stored oil but do not reduce significantly the emissions from stored gasoline.

Ordinary fixed-roof tanks normally are used to store less volatile petroleum products. Floating-roof vessels usually are used to store gasoline. All tanks may lose vapors at gauging hatches, sample hatches, and relief vents unless these points are designed and maintained for proper closure.[35] Fmissions of hydrocarbons (including benzene) from gasoline stored in a floating-roof tank occur primarily because of improper fit of the seal and shoe to the vessel shell, which exposes some liquid surface to the atmosphere.[117] Small losses also occur when vapor escapes between the flexible membrane seal and the roof and during withdrawal. Withdrawal losses result from evaporation of liquid from the tank wall as the roof descends during emptying operations.[117] 'Breathing' losses caused by the expansion and contraction of vapors promoted by diurnal changes in atmospheric temperature are primarily associated with fixed-roof tanks. Because of the low volume of gasoline stored in fixed-roof vessels, 'breathing' losses are not considered a significant source of ambient benzene.

Limited data have been reported on benzene exposures adjacent to storage facilities. A survey of industry by OSHA (April 1975) reported an average 375 ppm of benzene measured next to the sampling port atop a benzene storage tank.[48]

Total benzene emissions from gasoline storage are estimated on the assumption that all gasoline is stored in floating-roof tanks with typical capacities of 8700 $m^3$ (2.3 million gallons).[21] Applying emission relationships presented by Radian[117] yields estimated hydrocarbon losses of 132 lb/day per tank during storage (standing) and 0.025 $lb/10^3$ gallons during withdrawal. Emission factors given by Radian are based on American Petroleum Institute (API) data for floating-roof tanks. A subsequent study for the Western Oil & Gas Association (WOGA) of standing losses from floating-roof tanks found the hydrocarbon losses to be 58 percent of the API levels.[140] This lesser emission rate may not be representative of industry-wide practice; thus the API value will be utilized in calculations.

Our calculations are based on an annual domestic gasoline consumption rate of 378 $Mm^3$ (100 billion gallons).[67] It is assumed that the average tank retention (turnover) time is 30 days and the average tank is 75 percent full. The resulting annual hydrocarbon emissions are 25.46 Gg (55.4 million lb) for standing losses and 1.1 Gg (2.5 million lb) for working losses. Data presented by Runion[121] were applied to convert to benzene losses. The essentially linear relationship between benzene in gasoline and the vapor-phase benzene level is 0.4 x volume percent benzene in the vapor for each volume percent of benzene in the liquid. Utilizing the national average of 2 percent* benzene level in gasoline yields total annual benzene standing losses of 0.20 Gg (0.44 million lb) or working losses of 0.01 Gg (20,000 lb). The calculations are as follows:

---

* As developed in Section 4.1.

Gasoline storage standing losses =

$$\frac{(100 \times 10^{9})^{*}\ (365)^{+}}{(0.75)(2.3 \times 10^{6})^{\S}(12)^{+}} \times (132)^{\#} \times (0.02)(0.45)^{**} =$$

$= 0.77$ Gg/yr (1.70 million lb/yr).

and the benzene emission factor = $1.66 \times 10^{-4}$ lb/$10^{3}$ gal.

Gasoline storage withdrawal losses =

$$(100 \times 10^{9})^{**} \times \frac{(0.025)^{++}}{(1000)} \times (0.02)(0.45)^{**}$$

$= 0.01$ Gg/yr (20,000 lb/yr).

Benzene normally is stored in floating-roof storage tanks. Based on a typical storage tank having a capacity of 8700 $m^3$ (2.3 million gallon), the estimated corrected benzene emission rate would be 4.6 kg/day per tank (10.3 lb/day) for standing loss and 0.89 g/day per $m^3$ (0.0074 lb/day per $10^3$ gallon) for withdrawal loss.[140,117] On the basis of a 5.67 million $m^3$ (1.5 billion gallon) annual benzene consumption and a 30-day tank retention time, the annual benzene losses are 0.12 Gg/yr (0.26 million lb/yr) for standing and 5.0 Mg/yr (11,000 lb/yr) for withdrawal. The calculations follow:

---

[*] Annual gasoline usage, gallons/yr.[67]

[+] The tank emission factor is converted from lb/day to lb/year by assuming 12 fillings per year and a 30-day retention time.

[§] Average tank size determined from the 2701 terminals listed and total national gasoline storage capacity of 23.5 $Mm^3$ (6.2 billion gallons) for these terminals in 1967;[21] each tank is assumed to be 75 percent full.

[#] Gasoline emission, lb/day for this average tank.[117]

[**] Benzene conversion, 2 percent of gasoline and vapor-phase concentration at 40 percent of liquid concentration (converted to vapor weight basis, this is 45 percent).

[++] Withdrawal loss for gasoline, lb/$10^3$ gallon.[117]

Benzene storage standing losses =

$$\frac{(1.5 \times 10^9)^{*} \ (30)^{+} \ (10.3)^{\#}}{(0.75)\ (2.3 \times 10^6)^{\S}}$$

$= 0.12$ Gg/yr (0.26 million lb/yr).

and the benzene emission factor = 0.01 lb/day per $10^3$ gallon.

Benzene storage withdrawal losses =

$$\frac{(1.5 \times 10^9)^{*} (0.0074)^{**}}{(1000)} \quad 5.0 \text{ Mg/yr} = (11{,}000 \text{ lb/year}).$$

4.2.4.2 Crude Oil Operations - Benzene emissions from crude oil operations are based upon 0.15 lv percent of benzene in crude oil.[117] Radian reports a total evaporative hydrocarbon emission rate of 0.80 Gg/yr (1.77 billion lb/yr) from crude oil production and transportation.[117] If it is assumed that the benzene concentration in the hydrocarbons evaporated is 0.40 of the liquid, the benzene emission rate is 1.1 million lb/yr. Hydrocarbon emissions also result from storage of crude oil at the refinery. The estimated hydrocarbon emissions caused by standing in a fixed-roof, crude-oil storage tank with a diameter of 150 feet would be 798 lb/day per tank. Based on 0.15 lv percent benzene, 0.40 vapor/liquid concentration, and 4000 crude-oil storage tanks in use nationally, the total benzene emission rate is 0.3 Gg/yr (0.7 million lb/yr). Crude-oil working losses are estimated to be 3.53 lb hydrocarbons/1000 gallons oil.[117] Based upon a crude-oil consumption of 4.8 billion bbl/yr and the 0.15 lv percent benzene concentration in the crude, the

---

[*] 1976 benzene consumption, lb/year.

[+] 30-day retention time.

[§] Arithmetic average calculated from data on old and new tank operations, assuming tanks are typically 75 percent full.

[#] Tank emission factor, lb/tank-day.[117]

[**] Benzene withdrawal loss rate, lb/$10^3$ gal/day.

estimated benzene emission loss is 0.2 Gg/yr (0.4 million lb/yr.[18] Total benzene emissions from crude-oil operations are estimated to be 1.0 Gg/yr (2.2 million lb/yr). This is not considered an accurate estimate.[117]

4.2.4.3 Distribution - Distribution of gasoline from manufacturing facility to the consumer (service station, commercial user, etc.) is also a significant source of atmospheric benzene. An integrated network of pipelines, tank trucks, rail tank cars, barges, and ocean tankers connects intermediary storage and loading stations, as illustrated in Figure 4-9. Intermediate stations, termed "bulk terminals," are distinguished from stations supplied by tank vehicles, which are called "bulk plants." Service stations that fuel public motor vehicles are supplied by tank trucks from either bulk terminals or bulk plants. Privately owned commercial operations, such as those providing fuel for vehicles of a company fleet, are generally supplied by tank trucks from an intermediate bulk installation. Gasoline is loaded into the transport vehicles at bulk stations and refineries by means of loading racks.

Working losses, or vapors emitted during filling and emptying of tanks and tank trucks, occur at a rate directly proportional to the amount of gasoline charged to either vessel and to the rate of charging. Hydrocarbon emissions from tank truck loading racks are potentially much greater than emissions from bulk terminals.[21] As empty tank trucks are filled, hydrocarbons in the vapor space are displaced to the atmosphere unless vapor collection facilities have been provided. The quantity of hydrocarbons contained in the displaced vapors depends on the vapor pressure, temperature, method of tank filling, and conditions under which the truck was previously loaded. Figure 4-10 is a schematic drawing

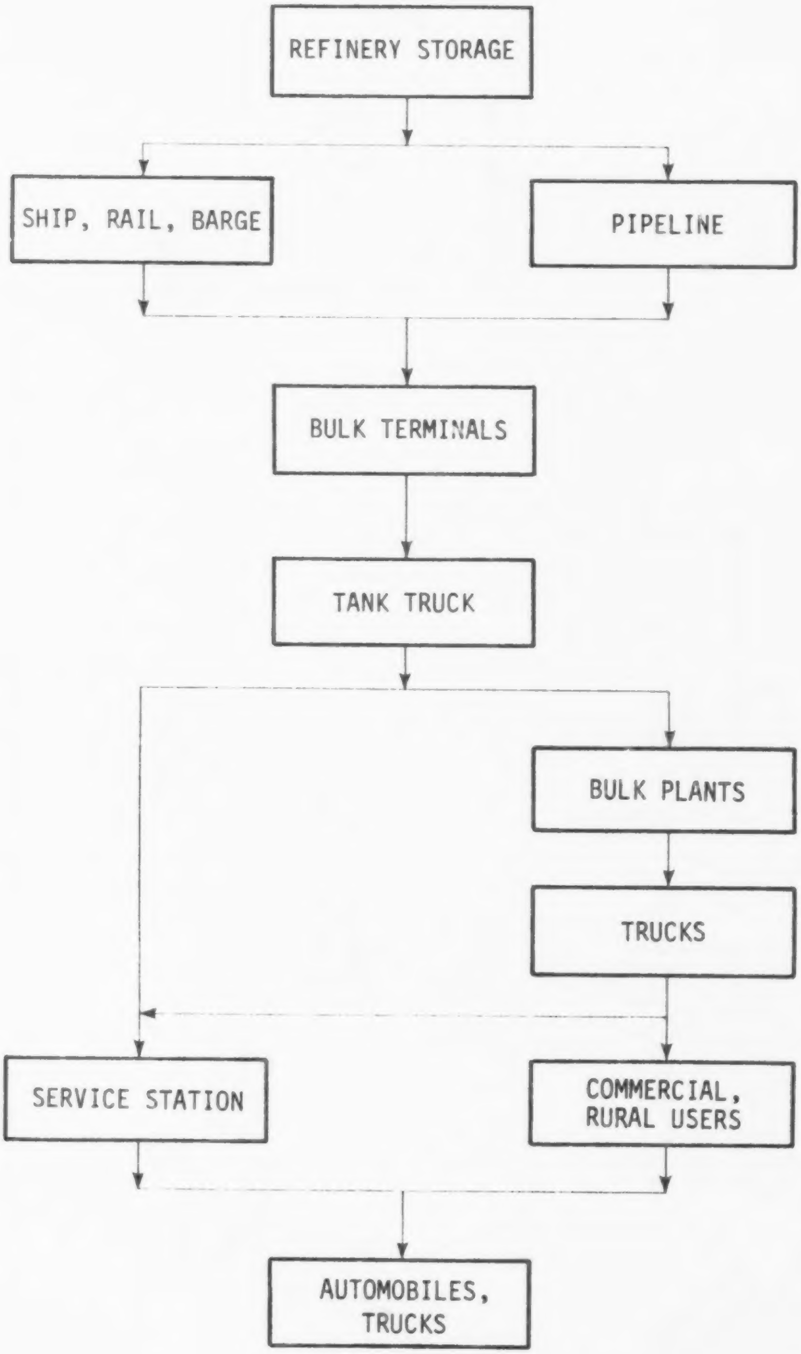

REFINERY STORAGE
SHIP, RAIL, BARGE
PIPELINE
BULK TERMINALS
TANK TRUCK
BULK PLANTS
TRUCKS
SERVICE STATION
COMMERCIAL, RURAL USERS
AUTOMOBILES, TRUCKS

Figure 4-9. The gasoline marketing distribution system in the United States.[21]

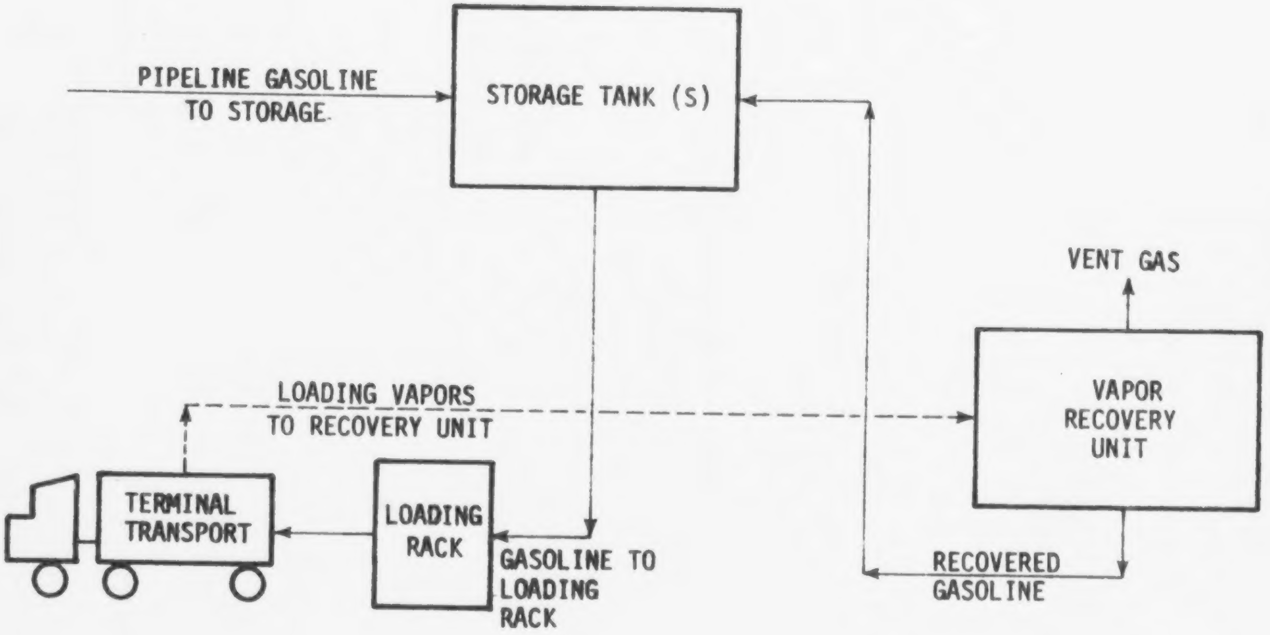

PIPELINE GASOLINE
TO STORAGE
STORAGE TANK (S)
VENT GAS
VAPOR
RECOVERY
UNIT
LOADING VAPORS
TO RECOVERY UNIT
TERMINAL
TRANSPORT
LOADING
RACK
GASOLINE TO
LOADING
RACK
RECOVERED
GASOLINE

Figure 4-10. Vapor and liquid flow in a typical bulk terminal (floating-roof tank).

Source: Ref. 21.

of liquid and vapor flow through a typical bulk terminal.

Exposures of workers to benzene were measured at several bulk loading installations in Britain (1969). Atmospheric benzene was measured by personal activated-charcoal samplers in 70 total determinations. Normal procedures for handling of gasolines with benzene contents ranging from 0.4 to 6.8 percent by volume resulted in ambient benzene concentrations ranging from 0.1 to 7.7 ppm; one sample showed 19.5 ppm. A 1972 study concerned benzene exposures during loading and weighing of rail tankers with gasoline from storage tanks. The mean concentration of benzene vapors escaping open tanker ports was 1.2 ppm, representing a time-weighted average over an 8-hour workday. The mean concentration of vapors drifting into the weighing room was 20 ppm on a time-weighted average basis. This exposure is equivalent to 14 ppm over an 8-hour workday.[49]

Gasoline is loaded from storage tanks to transport trucks (tank cars) by two basic methods: top loading and bottom loading. Top loading can be done by splash fill or submerged fill. In spash filling, the gasoline droplets undergo a 'free fall' and thus may evaporate or become entrained in the expelled vapors. In subsurface or submerged filling, the gasoline is introduced below the liquid surface in the tank. Bottom loading of gasoline is comparable to submerged top loading. Hydrocarbon emission factors have been developed to approximate the amount of uncontrolled gasoline vapor emitted by each of these loading operations.[21] Our calculations assume a 2.0 percent level of benzene in gasoline and a 0.45 factor* for the vapor benzene concentration based on the liquid benzene concentration.

---

* Shell Oil reports a benzene concentration in the hydrocarbon vapor of 0.1 weight percent for barge loading of gasoline containing 1.5 weighted percent benzene.[44]

Vapor containment efficiency of bottom-loading equipment may approach 100 percent if the truck or rail car has no leaks.[21] Although difficult to quantify, vapor collection efficiency for top loading is generally lower than for bottom loading.[21] An overall 95 percent efficiency of vapor recovery/containment is assumed for both loading and unloading.

It is assumed that half of the gasoline is transported by tank cars or trucks and half by marine vessels and that the loading of tank cars and trucks is 25 percent by the splash method and 75 percent by the submerged method. Table 4-10 presents estimated benzene emissions from gasoline transportation operations.

Table 4-10. ESTIMATED BENZENE EMISSIONS FROM GASOLINE TRANSPORTATION OPERATIONS

| Emission source | Uncontrolled emission factor[117] | Benzene emission rate, | |
|---|---|---|---|
| | | Gg/yr | (million lb/yr) |
| Loading-tank car/truck | | | |
| Submerged | 0.6 kg/$10^3$ ℓ<br>(5 lb/$10^3$ gal) | | |
| Splash | 1.4 kg/$10^3$ ℓ<br>(12 lb/$10^3$ gal) | | |
| Marine | 0.22 kg/$10^3$ ℓ<br>(1.8 lb/$10^3$ gal) | | |
| Loading total | | 0.43 | 0.96 |
| Transit | 0.4 kg/wk-$10^3$ ℓ<br>(3 lb/wk-$10^3$ gal) | 1.22 | 2.70 |
| Unloading | 0.26 kg/$10^3$ ℓ<br>(2.1 lb/$10^3$ gal) | 0.04 | 0.09 |
| Total | | 1.69 | 3.75 |

## Service Stations

Filling of underground gasoline storage tanks at service stations and service station operations together represent another source of evaporative benzene emissions. Emissions occur from displacement of hydrocarbon vapors to the atmosphere while the gasoline is being loaded into the storage tanks, underground tank breathing, and vehicle refueling operations. Estimates of benzene emissions from service stations are based on the rate of gasoline consumption and the benzene levels in gasoline presented earlier. Table 4-11 itemizes service station emissions. Storage tank filling and vehicle refueling are the largest sources. A percentage breakdown of the controls utilized in these operations is assumed, although no nationwide data are available to substantiate this assumption.

Within the past 2 years, Gulf Oil Corporation and others have monitored benzene exposure levels at service stations. In 1976 NIOSH conducted a brief study to determine potential exposure of attendants. The five service stations sampled were selected because of their large throughputs of gasoline and their location in a warm climate. Personal charcoal tubes were placed on the attendants. Most of the monitors indicated that benzene exposures were below detectable limits; some indicated concentrations ranging from 0.03 to 0.12 ppm.[64] A weighted average benzene content of the gasoline at the five stations was 1.24 lv percent.

A similar study of Gulf Oil service stations and marketing terminals, conducted in September 1976, showed an average benzene concentration of 0.32 ppm. The benzene content of the gasoline in this study was approximately 1.25 lv percent.

Service stations are now an important emission source category. As popularity of self-service operations increases,

## Table 4-11. INVENTORY OF SERVICE STATION BENZENE EMISSIONS

| Emission source | Hydrocarbon emission rate, $kg/10^3 \ell$ ($lb/10^3$ gal) throughput[117] | | Usage, % of total[a] | Benzene emission rate, Gg/yr (million lb/yr) |
|---|---|---|---|---|
| Filling tank | | | | |
| Submerged | 0.88 | 7.3 | 50 | |
| Splash | 1.38 | 11.5 | 25 | |
| Balanced | 0.04 | 0.3 | 25 | |
| | | | | 2.70 (5.95) |
| Underground tank breathing | 0.12 | 1.0 | 100 | 0.41 (0.90) |
| Vehicle refueling displacement losses | | | | |
| Uncontrolled | 1.08 | 9 | 75 | |
| Controlled | 0.11 | 0.9 | 25 | 2.85 ( 6.28) |
| Spillage[b] | 0.084 | 0.7 | 100 | 0.63 ( 1.40) |
| Total benzene emissions | | | | 6.59 (14.53) |

[a] These data represent estimated frequency of usage.

[b] All of the benzene in spillage is assumed to evaporate.

these operations could constitute a major source at which the population is exposed to benzene.

## Transport of Benzene

Benzene is transported principally by rail tank cars, tank trucks, and barges on inland waterways. As with gasoline, major emissions are assumed to occur during loading and unloading operations. These emissions may be generated by top (splash or submerged) and bottom loading of benzene into transit vehicles or by evaporative loss from spillage due to overfilling of tank cars or accidental discharge of benzene retained in transfer lines.[90]

In estimating emissions we assume that half the benzene is transported by tank car or truck and half by marine operations. Test data indicate a tank car/truck loading emission factor of 0.92 $lb/10^3$ gallon uncontrolled (we assume 95 percent control) and a marine loading emission factor of 1.5 $lb/10^3$ gallon.[117,44] These factors yield a total benzene loading loss of 0.34 Gg/yr (0.76 million lb/year). An assumed transit loss of 0.78 $lb/wk\text{-}10^3$ gallon leads to an annual emission of 0.53 Gg (1.17 million lb).[117] Emission data are limited, but in one instance disconnection of the hose at a loading point resulted in an exposure measurement of 75 ppm benzene.[48] During an industry survey, OSHA measured exposures at distances of 7, 15, 30, and 60 meters (25, 50, 100, and 200 feet) from loading facilities for tank cars, tank trucks, and barges.[48] In all cases exposure was reported to be less than 10 ppm over an 8-hour period. Depending on the transport means and distance from the loading point, short-term exposures ranged from zero to 60 ppm. Samples collected directly over hatch openings at barge and tank-truck loading ports showed average concentrations of 100 and 400 ppm, respectively.[90]

In summary, floating-roof tanks are normally used to store the more volatile petroleum fractions such as gasoline and benzene. Fixed-roof tanks are still used occasionally for gasoline storage, but they are being phased out. More atmospheric benzene is generated annually from gasoline storage than from benzene storage because a much higher volume of gasoline is manufactured. Crude oil operations may represent a significant source of benzene emissions, but reliable data are not available for estimating. Both benzene and gasoline are transported by tank truck, rail tank car, and marine vessel. This study indicates that in the handling and distribution of gasoline the greatest quantity of atmospheric benzene is emitted from underground storage tank filling and refueling of motor vehicle tanks at service stations. Lesser amounts are emitted during highly efficient, vapor-contained loading and unloading of bulk gasoline, as 'breathing' losses from service station underground tanks, and by evaporation of gasoline spillage. Table 4-12 presents benzene emission data and overall benzene emission factors for each source category.

### 4.2.5 Other Miscellaneous Sources

Hydrocarbons emitted because of incomplete combustion in fuel-burning equipment present a potential source of atmospheric benzene. Combustion efficiency governs the amount of hydrocarbon (and therefore benzene) emissions, and this efficiency depends on the operation and design of the combustion equipment. No emission data are available for this source.

Although still in the pilot stage, coal gasification plants present a definite potential for benzene emissions. The light-oil product from a Hy-Gas plant, a potential coal gasification process, contains about 8 percent benzene.[86]

## Table 4-12. SUMMARY OF BENZENE EMISSION FACTORS AND ANNUAL EMISSIONS FROM STORAGE/DISTRIBUTION OF GASOLINE AND BENZENE

| | Benzene emission factor, kg/$m^3$ (lb/1000 gal.) | Annual benzene emission, Gg ($10^6$ lb) |
|---|---|---|
| Storage | | |
| 1. Gasoline: standing | $3.3 \times 10^{-5}$ ($2.9 \times 10^{-4}$) | 0.8 (1.7) |
| Withdrawal | $2.6 \times 10^{-5}$ ($2.2 \times 10^{-4}$) | 0.0 (0.0) |
| Total | | 0.8 (1.7) |
| 2. Benzene: standing | $1.3 \times 10^{-5}$ ($1.1 \times 10^{-4}$) | 0.2 (0.5) |
| Withdrawal | $8.6 \times 10^{-4}$ ($7.4 \times 10^{-3}$) | (0.0) |
| Total | | 0.2 (0.5) |
| Crude oil operations | | |
| 1. Production and Transport | | 0.5 (1.1) |
| 2. Refinery storage - Standing | | 0.3 (0.7) |
| Withdrawal | | 0.2 (0.4) |
| Total | | 1.0 (2.2) |
| Distribution systems | | |
| 1. Gasoline losses | | |
| Loading | $1.1 \times 10^{-4}$ ($9.6 \times 10^{-4}$) | 0.4 (1.0) |
| Unloading | $1.1 \times 10^{-5}$ ($0.9 \times 10^{-4}$) | 0.0 (0.1) |
| Transit | 0.4/week (3.0/week) | 1.2 (2.7) |
| Total | | 1.7 (3.8) |
| 2. Benzene losses | | |
| Loading | $6.0 \times 10^{-5}$ ($5.1 \times 10^{-4}$) | 0.3 (0.8) |
| Unloading | low - unknown | low |
| Transit | 0.1/week (0.8/week) | 0.5 (1.2) |
| Total | | 0.9 (2.0) |
| Service Station Gasoline | | |
| Loading | $6.9 \times 10^{-3}$ ($5.9 \times 10^{-2}$) | 2.7 (6.0) |
| Refueling vehicles | $7.3 \times 10^{-3}$ ($6.3 \times 10^{-2}$) | 2.9 (6.3) |
| Underground tank breathing losses | $1.1 \times 10^{-3}$ ($0.9 \times 10^{-2}$) | 0.4 (0.9) |
| Gasoline spillage | $1.6 \times 10^{-3}$ ($1.4 \times 10^{-2}$) | 0.6 (1.4) |
| Total | | 6.6 (14.6) |
| TOTAL | | (24.8) |

Other potential sources of benzene emission include solid waste incineration, forest fires, structural fires, coal refuse fires, and agricultural burning. No data are available on benzene emissions from these sources.

Investigation into emission of atmospheric benzene from sanitary landfills appears warranted. In a March 1976 study conducted at a site where large quantities of chemical wastes were being dumped, measurements of ambient benzene ranged from trace amounts to 1.55 mg/m$^3$, depending upon proximity to the landfill.[72] Samples were taken both upwind and downwind of the site within an approximate 1-mile radius. A single measurement was made directly atop the dump mound adjacent to the liquid waste pits. Samples were analyzed by gas chromatography with mass spectrometry. Evaluation of the data showed that average benzene concentrations were higher downwind. Analysis of the single sample taken atop the mound gave a benzene concentration of 900 $\mu$g/m$^3$.

## 4.3 BENZENE EMISSION SOURCE CHARACTERISTICS

This subsection provides a brief summary of available data from major benzene emission sources. Table 4-13 presents benzene emission factors for major stationary sources of various capacities. Maleic anhydride plants and coke oven batteries have by far the highest emission factors.

Table 4-14 summarizes emission factors for other air pollutants from major benzene emission sources. This information is meager for many of the sources.

Table 4-15 presents estimated emissions of benzene and other pollutants from a typical facility using benzene as an intermediate. These data were developed by incorporating plant size and emission factors (where listed) from previous tables. The data show that maleic anhydride is the most significant individual source of emitted benzene and other pollutants.

## Table 4-13. STATIONARY SOURCE EMISSION CHARACTERISTICS - 1976 BASIS

| | Benzene emission factor, kg/kg $10^{-3}$ | Plant capacity, $10^6$ lb/yr | | Total no. of facilities nationally | Emission characterization |
|---|---|---|---|---|---|
| | | Largest | Average | | |
| Nitrobenzene | 7.0 | 310 | 100 | 9 | Point-absorber |
| Aniline | c | 200 | 100 | 7 | Fugitive |
| Ethylbenzene | | | | | |
| - Monsanto | 0.62 | 1865 | 550 | 19 | Scrubber-vent |
| - Alkar | | | | | |
| - Mobil/Badger | | | | | |
| Styrene | 1.50 | 1300 | 460 | 13 | Column vent, reactor emergency vent |
| Maleic anhydride | 96.7 | 105 | 50 | 9 | Product recovery scrubber |
| Cyclohexane | c | 85 | 45 | 10 | Fugitive |
| Cumene | 0.25 | 650 | 270 | 14 | Fugitive |
| Phenol-Cumene[a] | 1.5 | 500 | 200 | 14 | Oxid. vent, postoxidation condenser |
| Toluene | 1.2 | 135 | | | c |
| Benzene | 0.1 | 48 | | | c |
| Chlorobenzene | 3.5 | 300 | 100 | | c |
| o-dichl | 10.0 | 25 | 12 | | c |
| p-dichl | 7.2 | 60 | 25 | 13 | Chlorinator, PDCD rec. system |
| Solvent | c | | | c | Evaporation |
| Other nonfuel | d | | | d | |
| Refineries | Low | | | 248 | Fugitive |
| Coke ovens | $7.6 \times 10^{-2}$[b] | | | 66 | Primarily fugitive |

[a] Emission factors are for uncontrolled operations. Emission calculated for each process, assuming half of throughput was controlled at 95%.

[b] Based on coal charged to coke-oven batteries.

[c] Data unavailable.

[d] No overall value available.

Table 4-14. OTHER AIR POLLUTANTS EMITTED FROM BENZENE SOURCES

| Benzene source | Pollutant | Emission factor, kg/kg product | Reference |
|---|---|---|---|
| Gasoline-powered motor vehicles | $HC/CO/NO_x$ | | |
| Diesel heavy-duty vehicles | $HC/CO/NO_x$ | | |
| Benzene production sources | | | |
| Petroleum refineries | Mixed HC | | |
| | $SO_2$ | | |
| | Particulates | | |
| Coke-ovens | $SO_2$ | $4.0 \times 10^{-3}$[a] | 31 |
| | CO | $9.5 \times 10^{-4}$[a] | 31 |
| | $NH_3$ | $1.8 \times 10^{-4}$[a] | 85,94 |
| | $H_2S$ | $1.9 \times 10^{-4}$[a] | 85,94 |
| | HCN | $1.9 \times 10^{-5}$[a] | 85,94 |
| | $NO_x$ | $2.7 \times 10^{-5}$[a] | 85 |
| | Phenols | $2.5 \times 10^{-4}$[a] | 94 |
| | PNA particulates | [b] | |
| Benzene consumption sources | | | |
| Nitrobenzene | $NO_x$ | $9 \times 10^{-5}$ | 66 |
| | Nitrobenzene | [c] | 66 |
| Aniline | [d] | | |
| Ethyllienzene | [d] | | |
| Styrene | Toluene | $2 \times 10^{-4}$ | 105 |
| | Ethylbenzene | $2 \times 10^{-5}$ | 105 |
| | Styrene | $5 \times 10^{-5}$ | 105 |
| | Nonaromatic HC | $9 \times 10^{-5}$ | 105 |

[a] kg/kg of coal feed.

[b] No emission estimates available.

[c] Low level.

[d] No data on pollutant identification.

(Continued)

Table 4-14.(Continued).

| Benzene source | Pollutant | Emission factor, kg/kg product | Reference |
|---|---|---|---|
| Maleic anhydride | Formaldehyde | $6.3 \times 10^{-3}$ | 88 |
| | Formic acid | $2.1 \times 10^{-3}$ | 88 |
| | Maleic acid | $3.1 \times 10^{-3}$ | 88 |
| | Maleic anhydride | $3.2 \times 10^{-3}$ | 88 |
| | Xylene | $11.7 \times 10^{-3}$ | 88 |
| | Total HC | $106.6 \times 10^{-3}$ | 88 |
| | CO | $633.3 \times 10^{-3}$ | 88 |
| | $NO_2$ | $0.3 \times 10^{-3}$ | 88 |
| Cyclohexane | CO, sulphur | c | 66 |
| Cumene | Cumene | $7.3 \times 10^{-4}$ | 44 |
| | Formaldehyde | $1.3 \times 10^{-4}$ | 44 |
| | Acetaldehyde | $1.6 \times 10^{-5}$ | 44 |
| | Methanol | $1.6 \times 10^{-5}$ | 44 |
| Phenol | Acetaldehyde | $9.0 \times 10^{-4}$ | 105 |
| | Formaldehyde | $3.2 \times 10^{-3}$ | 105 |
| | Acetone | $1.2 \times 10^{-3}$ | 105 |
| | Ethylbenzene | $2.0 \times 10^{-4}$ | 105 |
| | Cumene | $2.0 \times 10^{-3}$ | 105 |
| | Methyl Styrene | $4.3 \times 10^{-4}$ | 44 |
| | Phenol | $1.2 \times 10^{-6}$ | 44 |
| | Mesityloxide | $5 \times 10^{-8}$ | 105 |
| | Toluene | $4 \times 10^{-5}$ | 105 |
| Chlorobenzene | d | | |

[a] kg/kg of coal feed.

[b] No emission estimates available.

[c] Low level.

[d] No data on pollutant identification.

(Continued)

## Table 4-15. ESTIMATED EMISSIONS FROM AN AVERAGE FACILITY USING BENZENE AS AN INTERMEDIATE

| Benzene source | Emissions | | | | |
|---|---|---|---|---|---|
| | Benzene, | | Other pollutants, | | |
| | Gg/yr | ($10^6$ lb/yr) | | Gg/yr | ($10^6$ lb/yr) |
| Nitrobenzene | | | $NO_x$ | 0.00 | (0.01) |
| | | | Nitrobenzene | b | |
| Aniline | a | | c | | |
| Ethylbenzene | 0.15 | (0.34) | c | | |
| Styrene | 0.31 | (0.69) | Toluene | 0.04 | (0.09) |
| | | | Ethylbenzene | 0.00 | (0.01) |
| | | | Styrene | 0.01 | (0.02) |
| | | | Nonaromatic HC | 0.02 | (0.04) |
| Maleic anhydride | 2.20 | (4.84) | Formaldehyde | 0.14 | (0.32) |
| | | | Formic acid | 0.05 | (0.11) |
| | | | Maleic acid | 0.07 | (0.16) |
| | | | Maleic anhydride | 0.07 | (0.16) |
| | | | Xylene | 0.27 | (0.59) |
| | | | Total HC | 2.20 | (5.33) |
| | | | CO | 14.37 | (31.67) |
| | | | $NO_2$ | 0.01 | (0.02) |
| Cyclohexane | a | | CO, sulfur | b | |
| Cumene | 0.03 | (0.07) | Cumene | 0.09 | (0.20) |
| | | | Formaldehyde | 0.02 | (0.04) |
| | | | Acetaldehyde | b | |
| | | | Methanol | b | |
| Phenol | 0.14 | (0.30)[d] | Acetaldehyde | 0.08 | (0.18) |
| | | | Formaldehyde | 0.29 | (0.64) |
| | | | Acetone | 0.11 | (0.24) |
| | | | Ethylbenzene | 0.02 | (0.04) |
| | | | Cumene | 0.18 | (0.40) |
| | | | Methyl Styrene | 0.04 | (0.09) |
| | | | Phenol | b | |
| | | | Mesityloxide | b | |
| | | | Toluene | 0.00 | (0.01) |
| Chlorobenzene | 0.16 | (0.35) | c | | |
| p-dichlorobenzene | 0.08 | (0.18) | p-dichlorobenzene | b | |
| | | | Chlorobenzene | b | |
| | | | Dichlorobenzene | b | |
| | | | $HC_1$, $Cl_2$ | b | |
| Detergent alkylate | a | | c | | |
| Solvent operations | a | | Toluene | a | |
| | | | Xylene | a | |
| | | | Other HC | a | |

[a] No emission estimates available.

[b] Low level.

[c] No data on pollutant identification.

[d] Phenol production from cumene assuming uncontrolled operation.

# 5.0 CONTROL METHODS

Specific information on the effectiveness of the control methods for benzene emissions is very limited. Thus, attention in this section is directed primarily to hydrocarbon control. Descriptions of methods are somewhat general. Hydrocarbon control on automobiles is achieved by positive crankcase ventilation, evaporative emission control, catalytic oxidation, and engine modification. Benzene vapors are recovered at stationary sources of benzene primarily by absorption or condensation.

## 5.1 EMISSION CONTROLS FOR MOBILE SOURCES

Although some data are available on the effectiveness of systems for direct control of benzene, extensive research has been aimed at control of hydrocarbons (HC). Thus, this section focuses on the effectiveness of HC control by systems now under development. Attention is given also to emission levels of carbon monoxide (CO) and nitrogen oxides ($NO_x$), because regulation of these emissions is mandatory and their control influences the level of HC and benzene control.

Emission control systems in use on current-model motor vehicles include positive crankcase ventilation (PCV), exhaust gas recirculation (EGR), evaporative controls, and catalytic oxidation systems. PCV and evaporative controls minimize hydrocarbon emissions at the source, whereas catalytic oxidation reduces hydrocarbon emissions in the exhaust by oxidizing unburned hydrocarbons. In addition, engine modifications are made to minimize formation of contaminants in the cylinders. These modifications include improved air/fuel mixing and distribution systems and alteration of ignition characteristics.

### 5.1.1 Catalyst Technology[113]

Several types of catalytic converters are in use or under development. The oxidizing catalytic converter, a device in the exhaust stream that stimulates oxidation of unburned fuel, changes HC and CO emissions into harmless carbon dioxide ($CO_2$) and water. The reducing type of catalytic system stimulates conversion of $NO_x$ into nitrogen gas ($N_2$). These two converters can be combined in a dual-bed system, as shown in Figure 5-1.

The third basic type of catalytic system is the three-way catalyst, which appears to be in an advanced state of development in California. In this system HC, CO, and $NO_x$ are converted in one catalyst bed.

Catalyst-engine matching has also been improved significantly by feedback control systems that closely control air/fuel ratios. Oxygen sensors respond to excess oxygen in the exhaust gases and signal the carburetor or the fuel injection system to control the air/fuel mixture.

Table 4-6 (subsection 4.1.1) shows how effective catalytic converters are in reducing hydrocarbon and benzene emissions. Total HC emissions range from 0.133 to 0.489 g/km (0.214 to 0.788 g/mile), with benzene emissions generally below 6 mg/kg (0.01 g/mile).[2]

### 5.1.2 "Lean Burn" Technology[113]

Engines calibrated for very lean air/fuel mixtures achieve low emissions of CO, HC, and sulfuric acid even without a catalytic system. An advanced form of "lean burn" technology would utilize various sensors, including an oxygen sensor, a mini-computer, feedback circuits to optimize spark timing, exhaust gas recirculation rate, air/fuel

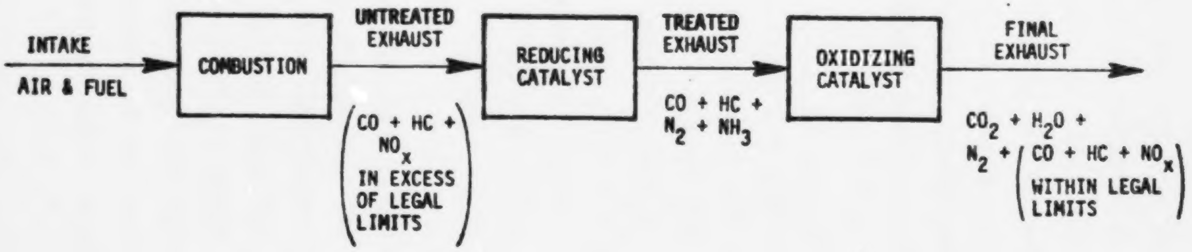

INTAKE
AIR & FUEL
COMBUSTION
UNTREATED EXHAUST
CO + HC + NO$_x$ IN EXCESS OF LEGAL LIMITS
REDUCING CATALYST
TREATED EXHAUST
CO + HC + N$_2$ + NH$_3$
OXIDIZING CATALYST
FINAL EXHAUST
CO$_2$ + H$_2$O + N$_2$ + (CO + HC + NO$_x$ WITHIN LEGAL LIMITS)

Figure 5-1. Operation of a dual-bed catalyst.

Source: Ref. 113.

ratio, and transmission shift points. These improvements might cost no more than current catalyst technology and would control emissions to the 1975 California levels ($HC/CO/NO_x$- 0.9/9.0/2.0 g/mile), with little or no loss of fuel economy as compared with uncontrolled cars. Reductions of emissions much below these levels will most likely require a catalyst in conjunction with some or all of the "lean burn" system components. One domestic manufacturer is actively considering full-scale production of lean-burn-type vehicles.

### 5.1.3 Exhaust Gas Recirculation[113]

Recirculating exhaust gas through the intake system controls $NO_x$ emissions by reducing the peak combustion temperature. The exhaust gas, an inert substance, does not contribute to the combustion process. Refinements of EGR systems have been made in the laboratory, the most significant recent work being that of Gumbelton.[113] He reports an EGR system yielding $NO_x$ levels of 0.62 g/km (1.0 g/mile) from full-size cars without fuel economy penalties. The conditions that promote low $NO_x$ levels, however, also promote high HC emissions. Achieving low $NO_x$ emissions can increase HC emissions to the point that 0.41 HC standard is more difficult to meet than the 0.4 $NO_x$ standard.

It is clear that optimum EGR operation will require more advanced systems than are currently available. Laboratory work on electronically modulated EGR and spark-timing systems has been reported as encouraging, but no commitments have been made to produce such systems.

### 5.1.4 Questor System[113]

The Questor system combines high-temperature oxidation of HC and CO with catalytic reduction of $NO_x$. This system has shown considerable potential for achieving the 0.41/3.4/0.4 standards. In tests of standard-size cars by several manufacturers, emissions were reduced below the standards. Problems remain, however, with the degree of mixture enrichment and the high temperatures required to achieve adequate control of HC, CO, and $NO_x$. The rich mixtures used with the Questor system increase fuel consumption and exhaust temperatures, causing degradation of the system with use. Over 3 years, however, the fuel economy associated with the Questor system has been improved to a position of parity with 1974 models (13% lower than in 1975 models).

### 5.1.5 Alternative Engines[113]

Several alternatives to the conventional internal combustion engine now under development may have some bearing on emissions in the next few years.

The stratified-charge engine uses a layered fuel mixture in the combustion chamber. The idea is to provide a fuel-rich mixture near the point of ignition in the cylinder while keeping the rest of the mixture lean.

Honda's CVCC stratified-charge engine has been shown to be capable of bringing even full-size cars into compliance with 0.41/3.4/2.0 standards with essentially no increase in fuel consumption over the total of average 1975 cars.

Ford's Proco stratified-charge engine uses an open combustion chamber different from the Honda prechamber system. The Proco can achieve $NO_x$ levels of 0.4 in 2.0-Mg (4500-lb) cars without catalytic control of $NO_x$ because of the combination of stratified-charge combustion and high EGR. HC emissions have presented the greatest problem. Although the Proco vehicle can simultaneously achieve 0.41/3.4/0.4 with oxidation catalysts, its HC emissions levels have exceeded 0.41 before 40,000 km (25,000 miles) at the 0.4 $NO_x$ calibration. Without controls, the Proco engine uses substantially less fuel than conventional engines, but the HC emissions are high. So far, reducing HC levels has required throttling, which makes the engine's fuel consumption comparable to that of conventional engines. Once throttling is used to control HC emissions, further measures to reduce $NO_x$ have little effect on fuel consumption. At present, there are no production versions of the Proco engine.

The rotary engine uses rotating drive elements to replace the reciprocating pistons of current internal combustion engines. In the past 5 years Toyo Kogyo has made major improvements in control technology for engines. Current prototypes of stratified-charge rotary engines show potential for meeting the 0.41/3.4/0.4 standards. Prototypes have achieved 0.33/1.7/0.38, while consuming less fuel than 1974 and 1975 production versions of the engine.

Diesel-engine passenger cars currently produced by several manufacturers show potential for meeting the 1978 standards for HC and CO. The automotive industry is studying greater use of diesel engines in passenger cars. It appears that diesel-powered passenger cars can be designed to achieve emission levels of 0.41 HC and 3.4 CO, with $NO_x$ levels in the range of 1.0 to 1.5. The prospects for meeting 0.4 $NO_x$ with a diesel automobile are not known but are considered unlikely.

Projects for development of Rankine cycle, gas turbine, and Stirling cycle engines have been initiated. Although these systems offer long-term potential for meeting very low emission standards, their large-scale manufacture will be later than that of the other systems discussed here, certainly after 1980.

### 5.1.6 Positive Crankcase Ventilation (PCV)[33]

PCV systems circulate air through the crankcase to pick up crankcase blowby gases and carry them to the intake manifold, where they enter the combustion chamber. The PCV system, as shown in Figure 5-2, is equipped with a control valve that restricts air flow when intake manifold vacuum is high but allows flow at idle conditions. In a closed system, the blowby gases, rich in hydrocarbons, are conducted to the air cleaner through the intake air hose. In an open system, the gases are vented to the engine compartment through the crankcase breather cap. When operating properly, these systems virtually eliminate hydrocarbon emissions, including benzene.

### 5.1.7 Fuel Evaporative Controls

Fuel evaporative control systems were installed on all 1971 model vehicles. Gasoline tanks and carburetors are the major sources of evaporative emissions. The most common control technique is the adsorption-regeneration system, which virtually eliminates evaporative hydrocarbon emissions, including benzene.

The vapor-recovery system, in which the crankcase is used as a storage volume for vapors from the fuel tank and carburetor, is not currently used.

In the adsorption-regeneration system, a canister of activated carbon traps the vapors and holds them until such time as they can be fed back into the induction system for burning in the combustion chamber. During a hot-soak period, vapor from the fuel tank is routed to a condenser and separator, and liquid fuel is returned to the tank. The remaining vapor, along with fuel vapor from the carburetor, is vented through a canister filled with activated carbon, which traps the fuel vapor. When the engine is started,

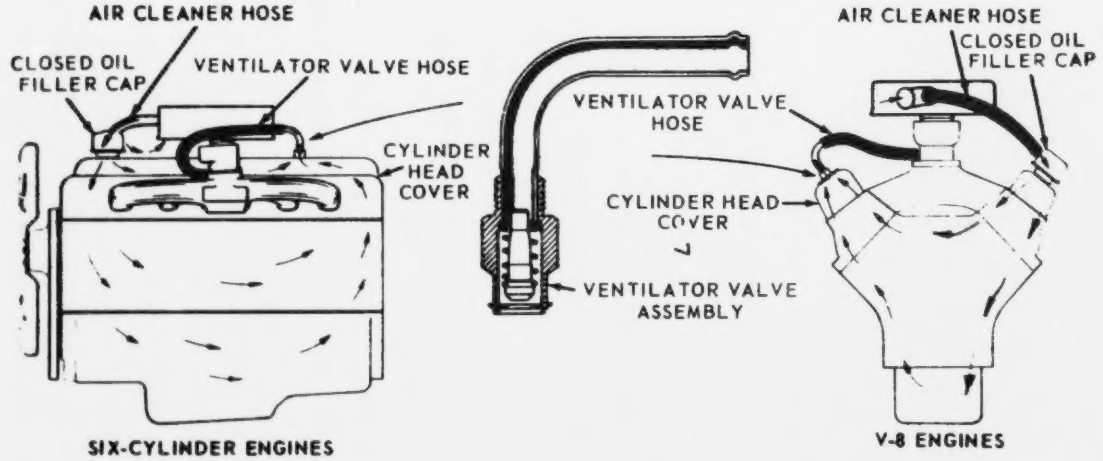

AIR CLEANER HOSE
CLOSED OIL FILLER CAP
VENTILATOR VALVE HOSE
CYLINDER HEAD COVER
SIX-CYLINDER ENGINES
VENTILATOR VALVE HOSE
CYLINDER HEAD COVER
VENTILATOR VALVE ASSEMBLY
AIR CLEANER HOSE
CLOSED OIL FILLER CAP
V-8 ENGINES

Figure 5-2. Closed positive crankcase ventilation system.

Source: Ref. 33.

fresh purge air drawn through the canister strips the activated carbon of the trapped fuel vapor and carries it to the combustion chambers.[33] Figure 5-3 shows a typical adsorption-regeneration system employing a three-way check valve.

The following excerpt summarizes results of a 1976 assessment of evaporative control systems by Exxon Research and Engineering Company.[30]

> A new test method, known as the SHED method, has shown that the evaporative emission controls in the field are less effective than originally estimated and in the case of some critical late model vehicles, evaporative emissions are of the same magnitude as the exhaust hydrocarbon emission....The average evaporative loss for a 20 car group was 8.7 grams/SHED test. The lowest loss was 0.5 gram and the highest was 30.6 grams.... Hardware was developed to improve ECS performance. Six vehicles were modified to demonstrate the feasibility of improving current systems. The modifications involved: (1) the venting of the carburetor bowl to the canister to alleviate air cleaner overflow, (2) utilization of larger carbon beds, (3) adaptation of increased purge rates, and (4) sealing and capping of leak sources. These modifications were successful in lowering the evaporative emissions to 2.0 grams/SHED test or lower for each of the six modified vehicles. We have concluded from this work that it is feasible to markedly improve the performance of current evaporative control systems.

### 5.1.8 Current Status of Mobile Emission Control

Table 5-1 presents a percentage breakdown of controls used on cars in operation in 1976.

Table 5-1. ESTIMATED USAGE OF CONTROL DEVICES ON CARS IN OPERATION IN 1976[95]

| Device | No. of cars | Percentage |
|---|---|---|
| Crankcase controls | 89,234,000 | 94 |
| Exhaust controls | 69,076,000 | 73 |
| Full evaporative controls | 45,213,000 | 47 |
| No controls | 3,998,000 | 4 |

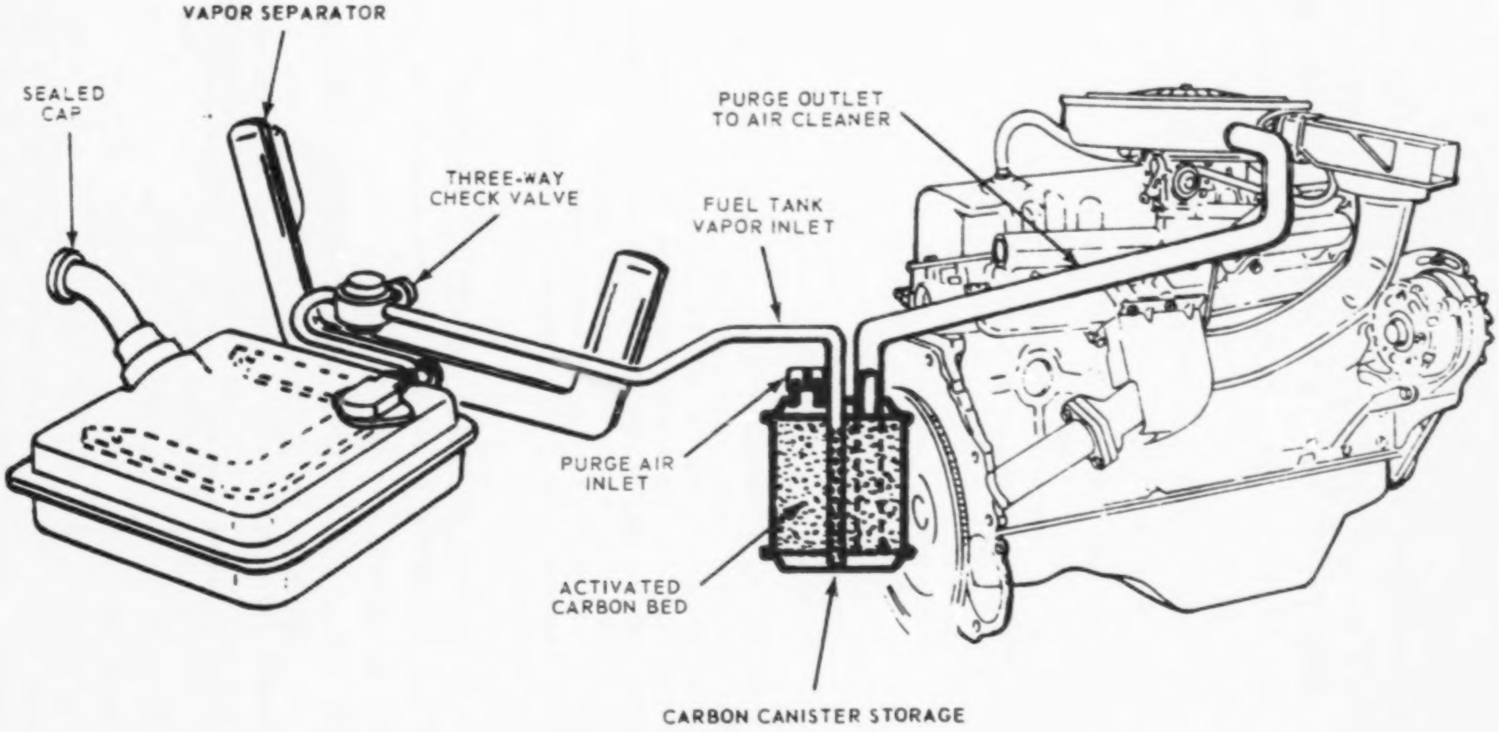

VAPOR SEPARATOR
SEALED CAP
THREE-WAY CHECK VALVE
FUEL TANK VAPOR INLET
PURGE OUTLET TO AIR CLEANER
PURGE AIR INLET
ACTIVATED CARBON BED
CARBON CANISTER STORAGE

Figure 5-3. Adsorption-regeneration evaporative emissions control system.
Source: Ref. 33.

## 5.2 EMISSION CONTROLS FOR STATIONARY SOURCES

In recent years, regulations on control of organic emissions from stationary sources have been limited to those compounds that are classified as photochemically reactive. Benzene is classified as a nonphotochemically reactive compound.

Benzene producers and consumers whose operations constitute distinct point sources of benzene (usually chemical reactors) usually recover vapors by absorption or condensation. However, recovery is for economic reasons and can be considered as part of the process rather than as an air-pollution control. When emissions involve occupational health hazards or local nuisances (odors), more stringent control of organic vapors (benzene) can be achieved by incineration or adsorption.

This section describes control of benzene emissions from gasoline distribution systems; coke ovens; and production of cumene, styrene, maleic anhydride, and paradichlorobenzene.

### 5.2.1 Status of Source Control

Little information is available on the usage of air pollution control devices in benzene-producing and -consuming industries. Table 5-2 indicates the typical emission controls for the major point sources of benzene in these industries.

The most common control systems in benzene production and the major processes using benzenes are absorption and/or condensation, which are practiced primarily to recover the valuable organic compounds.

Fugitive gaseous emissions from leaky valves and pumps and evaporative emissions from storage tanks and water

## Table 5-2. CONTROL METHODS FOR MAJOR POINT SOURCES OF ATMOSPHERIC BENZENE

| Product | Process | Control method |
|---|---|---|
| Nitrobenzene | Nitrator | Absorption with water |
| Aniline | Reactor | N/A |
| Ethylbenzene | Reactor | Condensor/absorption |
| Maleic anhydride | Hydrogenation reactor | Condensor/scrubber |
| Cyclohexane | Hydrogenation reactor | N/A |
| Phenol | Oxidizer | Multistage condensers with scrubbers, adsorption, or incineration |
| Chlorobenzene | Chlorinator absorption tower | Absorption with water |
| Paradichlorobenzene | | Wet scrubbers or absorption columns |
| Cumene | Oxidizer vent | Condensor |
| Styrene | Benzene-toluene recovery | Condensor or absorbers |
| | Primary distillation | Condensor |
| | Stripper vent | N/A |

N/A - Not available.

treatment and collection systems can be significant and generally are difficult to control.

### 5.2.2 Control Methods

Methods applied commercially to control organic emissions (benzene) and/or to recover valuable products are described in this section. Control measures include absorption, adsorption, condensation, and incineration.

Valves, pumps, and piping can release fugitive organic emissions in petroleum refineries and chemical processing plants as a result of leakage caused by vibration, heat, pressure, corrosion, and improper maintenance. Inspection and preventive maintenance can help to reduce these emissions. Also, some pump designs include special seals for minimizing leakage of volatile organic vapors.

By far the most important control technique is to design basic equipment so as to make the most efficient use of the materials being processed.

#### 5.2.2.1 Absorption[34]

Introduction - In the absorption process, a soluble component of a gas mixture is dissolved into a relatively nonvolatile liquid. In addition to being dissolved, the gas mixture may react chemically with the liquid. This technique is common and profitable in petroleum and petrochemical operations in which a gas includes a relatively high concentration of solvent vapor.

Absorption of hydrocarbons is an important manufacturing step in the petroleum and petrochemical industries. This type of absorption must be considered as a preliminary step in air pollution control, because it does not usually remove enough of the pollutant material to provide final control.

Common absorbents for organic vapors are water, mineral oil, nonvolatile hydrocarbon oils, and aqueous solutions (e.g., solutions of oxidizing agents, sodium carbonate, or sodium hydroxide). Trace benzene emissions are absorbed primarily with water; however, they sometimes are absorbed with toluene or ethanol.

Types of Absorbers - Gas absorption equipment is designed to provide thorough contact of the gas and the liquid solvent, enough to permit interphase diffusion of the materials. Contact is provided by several types of equipment: bubble-plate columns, jet scrubbers, packed towers, spray towers, and venturi scrubbers.

### 5.2.2.2 Condensation[34]

Introduction - Condensation and subsequent removal of organic compounds is a proven method of reducing organic emissions. At a given temperature, if the partial pressure of a compound is increased until it is equal to or greater than its vapor pressure at that temperature, the compound will condense. Alternatively, condensation will occur if the temperature of a gaseous mixture is reduced to a saturation point at which the vapor pressure equals the partial pressure of one of the constituents. In most air pollution control applications, condensation is effected by reducing the temperature.

Because of their relatively high boiling points, many organic compounds condense readily even though they are not highly concentrated. Benzene, however, has a relatively low boiling point of 80°C.

Condensers are applied widely in the organic chemicals industry to condense concentrated vapors in the primary process rather than to reduce contaminant emissions. Applied in the primary process, they allow recovery of valuable products.

Control of an organic emission by condensation is limited by the equilibrium partial pressure of the organic. Figure 5-4 shows a vapor pressure curve for benzene. As condensation occurs, the partial pressure of the material remaining in the gas phase decreases rapidly, making complete condensation impossible. For this reason, condensers usually must be followed by a secondary control system such as an afterburner, which combusts the noncondensible gases and provides a high degree of overall efficiency.

Condensers are of two types, surface and contact. In a surface condenser, the vapor to be condensed and the cooling medium are separated by a metal wall; in a contact condenser, the vapor and the cooling medium are brought into direct contact. Surface condensers include the common shell-and-tube heat exchangers. In these devices, the cooling medium, usually water, flows through the tubes, and vapor condenses on the outside surface. The condensed vapor forms a film on the cool tubes and drains to a vessel for storage or disposal. Air-cooled condensers are usually constructed with finned tubes, and the vapor condenses inside the tubes.

Contact condensers cool the vapor by spraying a cold liquid, usually water, directly into the gas stream. The condensed vapor and water mixture are then treated and disposed of or recovered. Contact condensers usually are less expensive, more flexible, and more efficient in removing organic compounds than surface condensers. Examples of contact condensers are the steam or water ejector and the barometric condenser, in which the condensing vapors create a negative pressure, inducing the flow of additional vapor from the process.

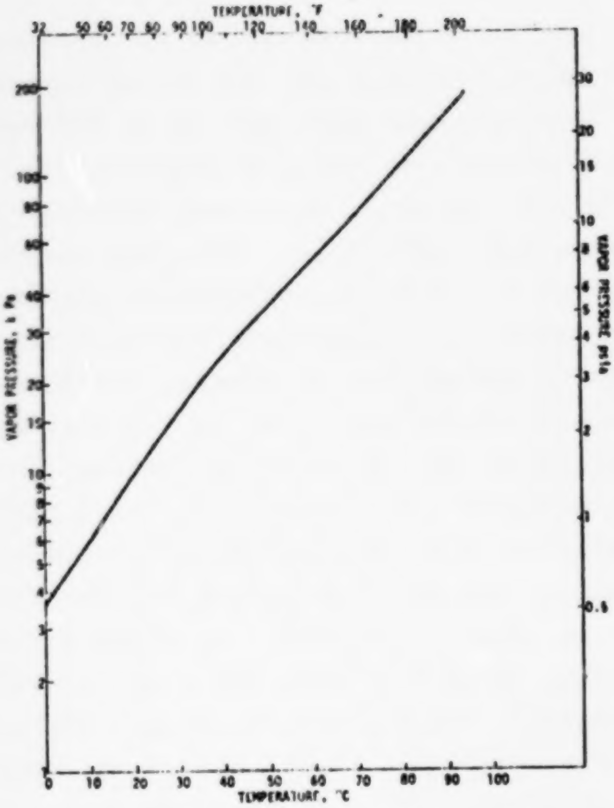


Figure 5-4. Vapor pressure of liquid benzene at various temperatures.

Source: Ref. 160.

The main design factors to be considered for condensation of organic compounds are the type(s) of compounds and their temperature, volume, concentration, vapor pressure, and specific heat. In streams containing a variety of hydrocarbon species, condensor design is based on the component with the highest boiling point.

5.2.2.3 Incineration[34] - Incineration controls organic emissions by combustion. The objective is to oxidize completely the organic vapors and gases emitted from a process or operation. Emissions, of course, include particulate as well as gaseous matter. Combustible particulates may be controlled by incineration. Incinerators are used widely and successfully for reducing organic emissions. They also offer potential for heat recovery.

Devices in which dilute concentrations of organic vapors are burned by addition of fuel are known as afterburners. Devices for burning of waste gases having enough heating value to burn without added fuel are known either as flares (if gases are not premixed with air) or incinerators (if gases are premixed with air). Combustion in afterburners is accomplished either by direct-flame incineration or by catalytic oxidation. Under the proper conditions, the firebox of a process heater or boiler may also be used as an afterburner.

Attempting to control organic vapors that contain halogens or sulfur by means of combustion alone is not considered wise because the combustion products of such materials are usually undesirable and often corrosive. Removal of these contaminants may require a secondary control system, such as a scrubber.

Properly designed and operated direct-flame afterburners usually achieve more than 95 percent efficiency in removal of organic vapors. Burner utilization must be considered in conjunction with the overall combustor design to achieve the optimum temperature and turbulence.

Catalytic afterburners are much like direct-flame types, but they provide a solid active surface on which the combustion reaction takes place, usually at a significantly lower temperature than is required for combustion by direct flame. Because they can be operated at much lower temperatures and are self-sustaining, catalytic afterburners offer the advantage of lower fuel costs in some applications. Fuel requirements for a direct-flame afterburner can be reduced by means of a heat exchanger, however, and the total cost of operating a direct-flame afterburner then may be comparable to the cost of operating the catalytic type. The primary problems with catalytic afterburners are relatively high maintenance costs and catalyst deactivation by feed contaminants. These devices will not function if the catalyst becomes fouled by particulate matter or coated by polymers. Catalytic incineration typically reduces emissions 95 percent or more.

An afterburner that does not achieve substantially complete combustion of the organic emissions can produce CO, aldehydes, and other partially oxidized substances, which may be more objectionable than uncontrolled emissions.

5.2.2.4 Adsorption[34] - The condensation and retention of a gaseous or liquid substance on a solid surface is known as adsorption. Gas-purification processes involving this principle are based upon the physical properties of certain granular solids, known as adsorbents. These adsorbents attract selected components of a fluid to their surfaces and retain them there. Certain materials, such as activated alumina, silica gel, and activated carbon, have been developed to adsorb substantial quantities of gases and liquids. These materials are highly porous, with very high ratios of surface to volume. A liquid can penetrate the material and contact the large surface area available for adsorption. Complete package adsorption systems are available from a number of manufacturers.

In vapor-phase adsorption (essentially an exothermic gas-solid equilibrium process), the approach to equilibrium is governed by the rate of adsorption. Conditions that shift the equilibrium toward saturation usually improve the process. Consequently, the system is more efficient near the dew point of the adsorbate (substance being absorbed), and a vapor-phase adsorption system generally should operate at the highest pressure and the lowest temperature within the process limitations.

After some period of usage, the adsorbent becomes saturated with the contaminant and will no longer function. When this occurs, it must be regenerated or replaced. Regeneration may be done in a number of ways. The most common method is to withdraw the adsorbed gas in a stream of easily condensible gas such as steam. The stripped gas is then recovered by condensing the mixture. Thus, the adsorbent is restored to activity, and the adsorbed material is removed for disposal or recovery.

If the gases or vapors to be adsorbed consist of several compounds, adsorption of the various components is not uniform. Generally, these components are adsorbed in an approximately inverse relationship to their volatilities.

Although fixed-bed adsorbers generally are not installed to recover organic solvent vapors when the vapor-laden stream contains less than 0.2 pound of solvent per 1000 scf of gas (2700 ppm), they can recover much lower concentrations very efficiently. The reason is that adsorption is virtually complete and independent of concentration; however, the maximum bed loading (saturation point) is dependent on initial concentration.

In a certain range of vapor concentration (from a few ppm to about 1000 ppm), organics cannot be recovered profitably with either regenerative or nonregenerative adsorption. In this range, adsorption is often unsuitable for nonregenerative systems because of the high cost of adsorbent replacement. It is also uneconomical for regenerative systems because costs of adsorbate recovery generally exceed the value of the material recovered. For materials within such a range, newly developed oxidative destruction of the adsorbate can be applied instead of desorption. The carbon is impregnated with a small amount of catalyst, which is inactive during adsorption. It may be activated by heating the air stream and bringing about catalytic oxidation of the adsorbate.

For satisfactory adsorption, the molecular weight of a substance should be greater than 45. Benzene easily meets this requirement with a molecular weight of 78. Despite its disadvantages, adsorption appears to be the most economical method for control of organic vapors in the concentration range of 100 to 200 ppm, virtually eliminating the emissions.

Adsorbers may be classified as regenerative or nonregenerative. Regenerative systems are used when the adsorbent is to be reactivated by desorption and the desorbed vapors recovered for reuse or disposal. Nonregenerative systems are used when the adsorbent is to be replaced with fresh materials; the displaced material is returned to the vendor for regeneration or is discarded.

The use of silica gel and aluminum oxide is limited to dry streams because they preferentially adsorb water from a gas mixture containing water vapor and organic solvents. Thus their use in emission control is restricted because the water content of a gas stream is often greater than the organic vapor content. Silica gel and activated alumina disintegrate in the presence of liquid water; hence a wet steam cannot be used for desorption.

A typical adsorption process is depicted in Figure 5-5. One adsorber handles the vapor-laden stream while the other is undergoing regeneration. When the first, or onstream, adsorbent bed approaches the breakpoint, the second adsorber, which had undergone regeneration, is placed on stream. This procedure ensures that the vapor is removed from the air continuously.

Adsorbers can be used in fixed, moving, or fluidized beds and can be set vertically or horizontally. A single fixed-bed unit is satisfactory if the adsorbent can be regenerated during process downtime. For example, an adsorber for a spray-paint booth that is in use only 6 hours a day can be designed to extract the total emission during the spray operation for desorption later.

The simplest fixed-bed adsorber is a vertical cylindrical vessel fitted with perforated screens that support the carbon. In another type the beds are arranged in the shape of a cone, as shown in Figure 5-6. The cone shape allows more surface area for gas flow and accommodates higher air rates at lower pressure drops than does a flat

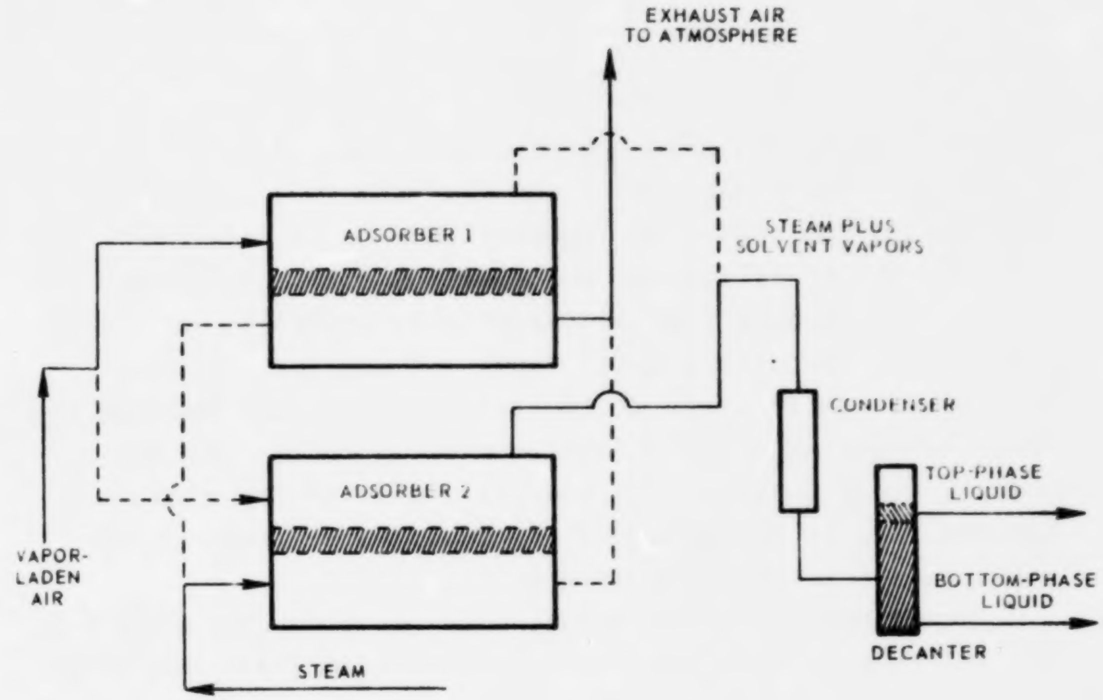

EXHAUST AIR
TO ATMOSPHERE
ADSORBER 1
STEAM PLUS
SOLVENT VAPORS
CONDENSER
ADSORBER 2
TOP-PHASE
LIQUID
VAPOR-
LADEN
AIR
BOTTOM-PHASE
LIQUID
DECANTER
STEAM

Figure 5-5. Two-unit fixed-bed adsorber.

Source: Ref. 34.

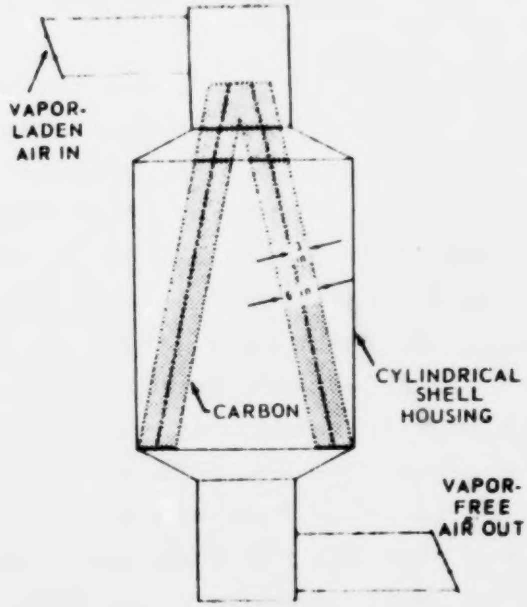

VAPOR-
LADEN
AIR IN
CARBON
CYLINDRICAL
SHELL
HOUSING
VAPOR-
FREE
AIR OUT

Figure 5-6. Vertical adsorber with two cones (permitting studies on different depths of carbon beds).

Source: Ref. 34.

bed of the same diameter using the same total weight of adsorbent. Where the cone shape will provide adequate adsorption, its use tends to reduce costs of moving the gases through the system.

Moving-bed adsorbers move the adsorbent into and out of the adsorption zone. The fluidized-bed adsorber contains a number of shallow beds of activated adsorbent. As the air flows upward through these beds and fluidizes them, the solvent is progressively adsorbed onto the carbon. An adsorption isotherm for benzene adsorption on activated coconut charcoal is given in Figure 5-7.

### 5.2.3 Control of Emissions from Distribution Systems

5.2.3.1 Bulk Terminal Storage[35] - Emission control technology for bulk terminals is the most highly developed in the gasoline marketing industry. For many years, certain regions have required emission controls at bulk terminals; additionally, the petroleum industry has viewed control of losses at bulk terminals as an economical means of conserving valuable fuel products.

Uncontrolled storage tanks can account for half of the gasoline emissions from a bulk terminal. Tankage losses occur from breathing, evaporation, filling, emptying, and wetted walls. The best technology for control of tankage losses consists of (1) floating a rigid cover on the surface of the stored gasoline to eliminate the vapor space and (2) containing the tankage vapors within a sealed system that incorporates a variable vapor space tank to provide surge capacity. The efficiency of these two approaches to controlling tankage emissions is greater than 90 percent (over uncontrolled tankage losses). The value of recovered gasoline has justified the cost of these tankage control systems.

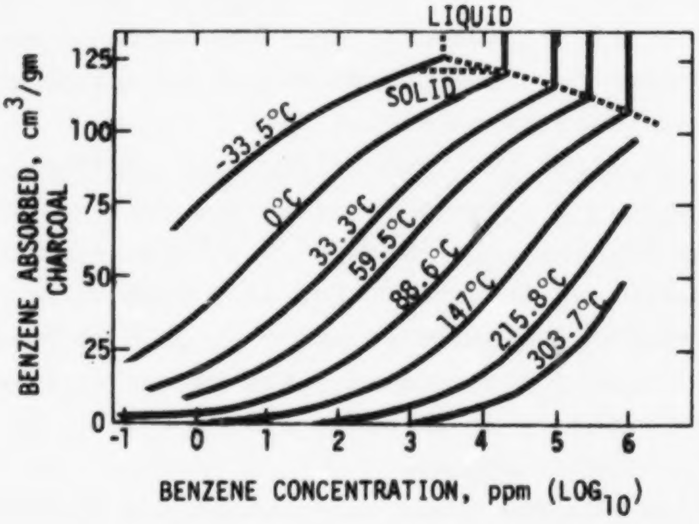


Figure 5-7. Adsorption of benzene on activated coconut charcoal at atmospheric pressure, out-gassed at 550°C.

Source: Ref. 69.

5.2.3.2 Loading Facilities - Gasoline and petrochemicals are distributed to the consumers by pipeline, trucks and trailers, railroad tank cars, and marine tankers, which can be deployed in various combinations to form a distribution system. Significant emissions of hydrocarbons (benzene) in these operations occur when gasoline or other hydrocarbons are loaded into tank trucks or stationary tanks. These operations and their emissions are described in Section 4.2.4. This section describes the control methods currently used.[34]

Overhead Loading[34] - Four types of vapor collectors have been developed for use during overhead loading operations. All are essentially plug-shaped devices that are inserted into a fitting for the hatch opening. Gasoline flows through a central channel in the device into the tank compartment. This central channel is surrounded by an annular space into which vapors enter through openings on the bottom of the hatch fitting. The annular space is in turn connected to a hose or pipe leading to a vapor disposal system.

A device developed by the Mobil Oil Corporation is connected to a vapor chamber with a transparent section to allow the operator to see the calibrated capacity markers in the tank compartment. Height of this closure is adjustable. Constant downward force is required to keep it firmly in place during filling. This device is built to fit only hatches 20 to 25 cm (8 to 10 inches) in diameter.

The Chiksan device incorporates the hatch closure, the vapor return line, and the fill line into an assembled unit. This unit incorporates features that prevent overfills, tipping off, or filling when the assembly is not properly seated in the tank hatch.

The Greenwood vapor closure, developed by the Vernon Tool Company, also requires downward force during filling and ordinarily does not include a transparent vapor chamber. This closure can be fitted with an adapter for hatches larger than 25 cm (10 inches).

The SOCO device, developed by Standard Oil Company of California, has a positive clamp for the hatch opening, which automatically actuates the vapor chamber when closed. The device also includes a safety shutoff float that senses the gas level and prevents overfilling. This device can be used with an adapter for hatches larger than 20 cm (8 inches) in diameter.

The slide positioner of the Mobil Oil Corporation device can allow leakage of vapors and requires close attention by the operator during adjustments for fitting and submerged loading. The inner valves of the SOCO device make it considerably heavier than the other types. This device increases pressure drop and reduces the loading rates. Mobil and Greenwood devices both require check valves in the vapor-gathering lines to prevent the vapor from discharging back to the atmosphere when the assembly is withdrawn. They also require nearly vertical entry of the loading tube into the hatch opening to ensure a tight seal against vapor leaks. An assembly is available that maintains the Greenwood device in the vertical position.

Bottom Loading[34] - Bottom loading facilitates collection of displaced vapors because the filling line and the vapor collection line are independent of each other. The vapor collection line consists of a flexible hose or swing-type arm connected to a quick-acting valve fitting on the dome of the vehicle. The vapor collection line must be equipped with a check valve to prevent backflow of vapors to the atmosphere when the connection to the tank is broken.

Vapor Disposal - Vapors collected during loading operations may be used as fuel or may be recovered as a product. When fired heaters or boilers are available, the displaced vapors may be directed through a drip pot to a small vapor holder, which is gas-blanketed to prevent formation of explosive mixtures. The vapors are drawn from this holder by a compressor and discharged to the fuel gas system.[34]

If the loading facility is near a refinery, the vapor line can be connected from the loading facility to an existing vapor recovery system through a regulator valve. If not, packaged units may be used to recover vapors. Figure 5-8 shows an absorption unit developed by the Superior Tank and Construction Company. It includes a tank equipped with a flexible membrane diaphragm, a saturator, an absorber, compressors, pumps, and instruments. These units use the gasoline product as the absorbent. Accumulation of explosive mixtures is prevented by passing the vapors displaced at the loading rack through a saturator countercurrently to gasoline pumped from storage. The saturated vapors then flow to the vaporsphere, where a diaphragm controls a compressor, which draws the vapors from the sphere and injects them at about 14 $kg/cm^2$ (200 $lb/in.^2$) into the absorber. Gasoline used to absorb the hydrocarbon vapors is returned to storage, whereas the remaining gases, mostly air, are released to the atmosphere through a backpressure regulator. Some difficulty has been experienced with air entrained in the gasoline returning to storage. Any such air released in the storage tank is saturated with hydrocarbon vapors as it is discharged. This air can be

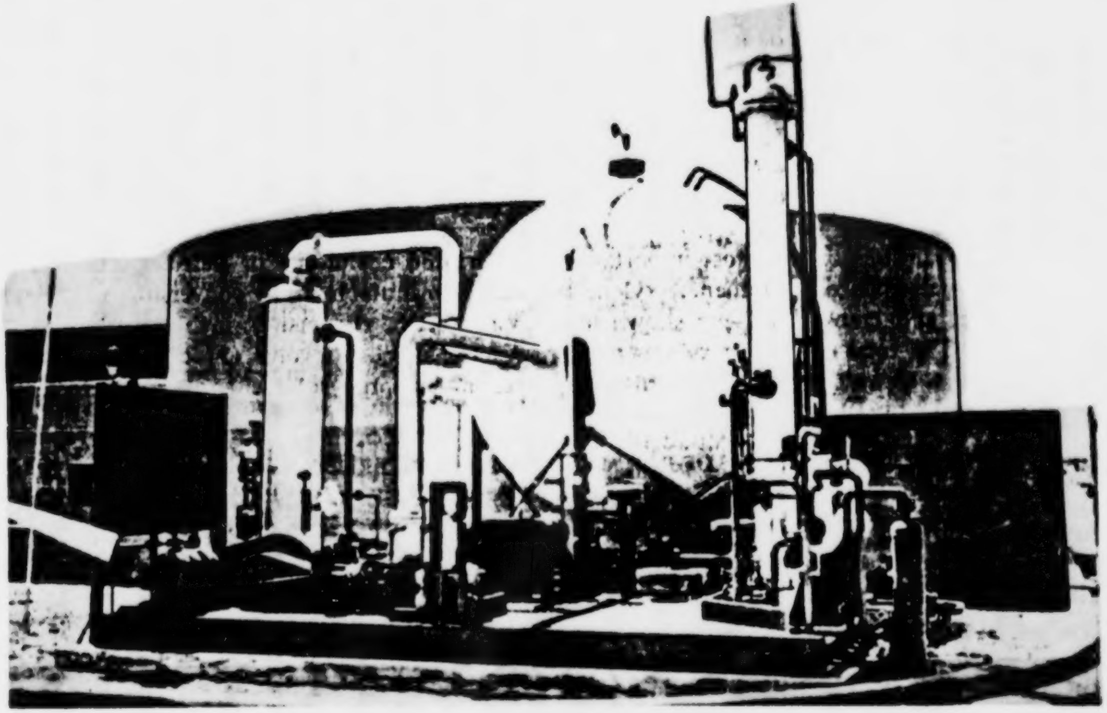


Figure 5-8. Small-capacity vaporsaver gasoline absorption unit.

Source: Ref. 35.

properly removed by flashing the liquid gasoline from the absorber in one or more additional vessels operating at successively lower pressures.[34]

In 1972, a comparison was made of alternative gasoline vapor control systems installed on gasoline-loading terminals.[164] Since none of the systems, hydrocarbon oxidation, absorption, or adsorption, could be justified economically, selection of the best system was based on recovery efficiency, demonstrated performance, and ability to meet air quality standards. Hydrocarbon oxidation is preferred for terminals pumping less than 3 million barrels per year. For larger terminals, a recovery system using an activated carbon adsorption unit in series with a conventional absorption column may be preferred. Tests performed on these systems show that hydrocarbon oxidation will effectively reduce emissions by 90 percent or more.

### 5.2.4 Control of Emissions from Coke Ovens

Major effort is currently being expended to control coke-oven emissions, primarily because of concern over their polynuclear aromatic constituents. It is believed that use of advanced technology could significantly reduce benzene emissions from the coke ovens.

A procedure commonly used to reduce emissions during coal charging is termed "charging on the main." A steam ejector in the ascension pipe produces a draft in the oven during the charging period, which causes the gases to be pulled into the gas collector main. Although it has undergone some improvements, this technique is generally considered to be ineffective. The two most feasible improvements are charging on the main with closed coal ports and pipeline charging. Charging on the main with closed coal ports can be readily incorporated into an existing plant. Features of this system include sequencing of coal charging from the larry car with charging port lids off only during charging, maintenance of a steady negative pressure in the oven, and continual drawoff of evolved gases. Pipeline charging involves preheating coal to drive off moisture and transporting it by pipeline. Although a 40 to 50 percent increase in oven capacity can be realized with this method, it is considerably more expensive, requiring far more extensive equipment changes than charging on the main with closed coal ports. Furthermore, the capacity of the byproduct recovery system must be increased to utilize the increase in oven capacity.

Several systems have been considered for control of emissions resulting from the discharge of newly produced coke. One system recently put in operation consists of an enclosed quench car, which is attached to a second car that carries a wet scrubber unit. During the pushing operation, emissions are collected in the hood and withdrawn through the coupled duct work between the cars to the wet scrubber unit.[103]

### 5.2.5 Control of Emissions from Sources Using Benzene

5.2.5.1 Styrene - The major source of benzene emissions in the production of styrene is from the benzene-toluene recovery columns. One column emits $4.2 \times 10^{-3}$ kg HC/kg styrene, consisting mainly of benzene and toluene. Columns are controlled by condensors or absorbers.[68]

Stripper vents, another major source, have been reported to emit $3.2 \times 10^{-3}$ kg ethylbenzene/kg styrene in one plant.[68] Stripper vents can be controlled by conventional methods discussed previously.

Benzene emissions from distillation columns are controlled well by vapor recovery systems. At one plant, primary distillation is controlled by a condensor and emits $0.4 \times 10^{-3}$ kg benzene/kg styrene. At another plant, primary distillation emits an uncontrolled 1.85 kg benzene/kg styrene.[68]

5.2.5.2 Cumene - The oxidizer vent is a major source of benzene emissions in the manufacture of cumene. At one plant, about $1.5 \times 10^{-3}$ kg benzene/kg of cumene is emitted from a condensor operating at 73 psig.[68] At another plant, emissions from the condensor are reduced to only 0.004 lb benzene/ton cumene.[68]

5.2.5.3 Maleic Anhydride (MAN) - The product recovery condensor vent is the most significant source of atmospheric benzene emissions in maleic anhydride manufacturing.[88] The uncontrolled emissions from a condensor are in the range of 0.06 to 0.20 kg benzene/kg MAN.[88] Condensors are vented to a scrubber to recover the MAN vapors. The uncondensed MAN vapors can also be controlled effectively by incineration in series with the wet scrubber. This system has been shown to practically eliminate hydrocarbons (including benzene) in the off gas.[88]

5.2.5.4 Paradichlorobenzene - Wet scrubbers and absorption columns are the most common benzene control devices used in paradichlorobenzene production. A single wet scrubber controls 90 percent of the benzene emissions and a single absorption column, 95 percent.[97]

## 5.3 CONTROL COSTS

This section discusses approximate capital and annual costs for controlling gaseous emissions, including benzene. The costs presented are limited to control devices and major auxiliary equipment; they do not include duct work, hoods, and stacks because these costs can be determined only on a case-by-case basis.

Cost figures cover absorption columns, carbon adsorbers, catalytic incinerators, and thermal incinerators. Because condensors are generally considered process equipment, they are not discussed here.

### 5.3.1 Absorption Columns

Purchase costs for absorption columns were obtained from a vendor.[146] They correspond with flow rates, as shown:

| Flow rate, scfm | Cost, \$ (mid-1976) |
|---|---|
| 22,600 | 14,200 |
| 28,400 | 17,500 |
| 41,000 | 27,300 |

These costs include the basic column with internal piping and packing. Construction is of fabricated reinforced polyethylene or carbon steel. Bed depth is 5 feet. The costs do not include pumps, fans, or instrumentation. The equation relating these costs to the flow rate is as follows:

$$\text{Purchase cost, \$} = 0.231\ Q^{1.1}$$

$Q$ = volume, scfm

This equation applies to packing bed depths of 5 feet and flow rates between 10,000 and 80,000 acfm.

Costs of deeper beds (giving higher efficiency) increases according to the following equation:[146]

$$\text{Purchase cost, \$} = 0.231\ Q^{1.1}\ (1 + 0.05\ [Z-5])$$

$Q$ = volume, scfm

$Z$ = bed depth, ft.

One other major system cost is the fan. The pressure drop through the bed (tellerette rings) is 0.4 to 0.6 in. WG per foot of packing.[146] Assuming 1 in. WG pressure drop through the rest of the system, the following equation relates bed depth and flow rate to fan size in horsepower:

$2.6 \times 10^{-4} (1 + 0.5 z) Q$ = fan size, hp

Fans in this size range can be purchased for $75 to 100 per horsepower, including base, motor, and drive.

Feed pump costs are insignificant in relation to those of the column and fan.

Total installed costs are usually 3.4 to 4.7 times the equipment purchase costs.[80] This factor includes not only direct installation costs but also engineering, tax, freight, and contingencies.

Annual operating costs include power, maintenance, labor, and fixed costs. Power costs are insignificant in relation to total annual costs.

Maintenance costs are assumed at 5 percent of the total installed costs (TIC). Labor is assumed at 0.1 man-hour/hour operation at $10/man-hour. Capital charges are 12 percent of TIC; taxes, insurance, etc. are about 4 percent of TIC.

Annualized costs can be roughly estimated by the following equation:

Annualized costs, $ = 0.24 (TIC) + 1.0 H

TIC = total installed cost, $

H = hours of operation per yr

### 5.3.2 Carbon Adsorption

Carbon adsorption units for benzene removal are designed for 0.06 kg benzene per kg carbon.[80] For example, a gas stream discharging 45.4 kg/hr (100 lb/hr) benzene would require 757.5 kg (1670 lb) carbon (density ~ 0.48 g/cc or 30 lb/ft$^3$) regenerating every hour. Beds are designed at 60 to 100 fpm superficial bed velocity and are 15 to 25 inches deep.

Costs of adsorption units are based on the weight of carbon. Figures 5-9 and 5-10 show total purchase prices for carbon adsorption systems, including fan, controls, and

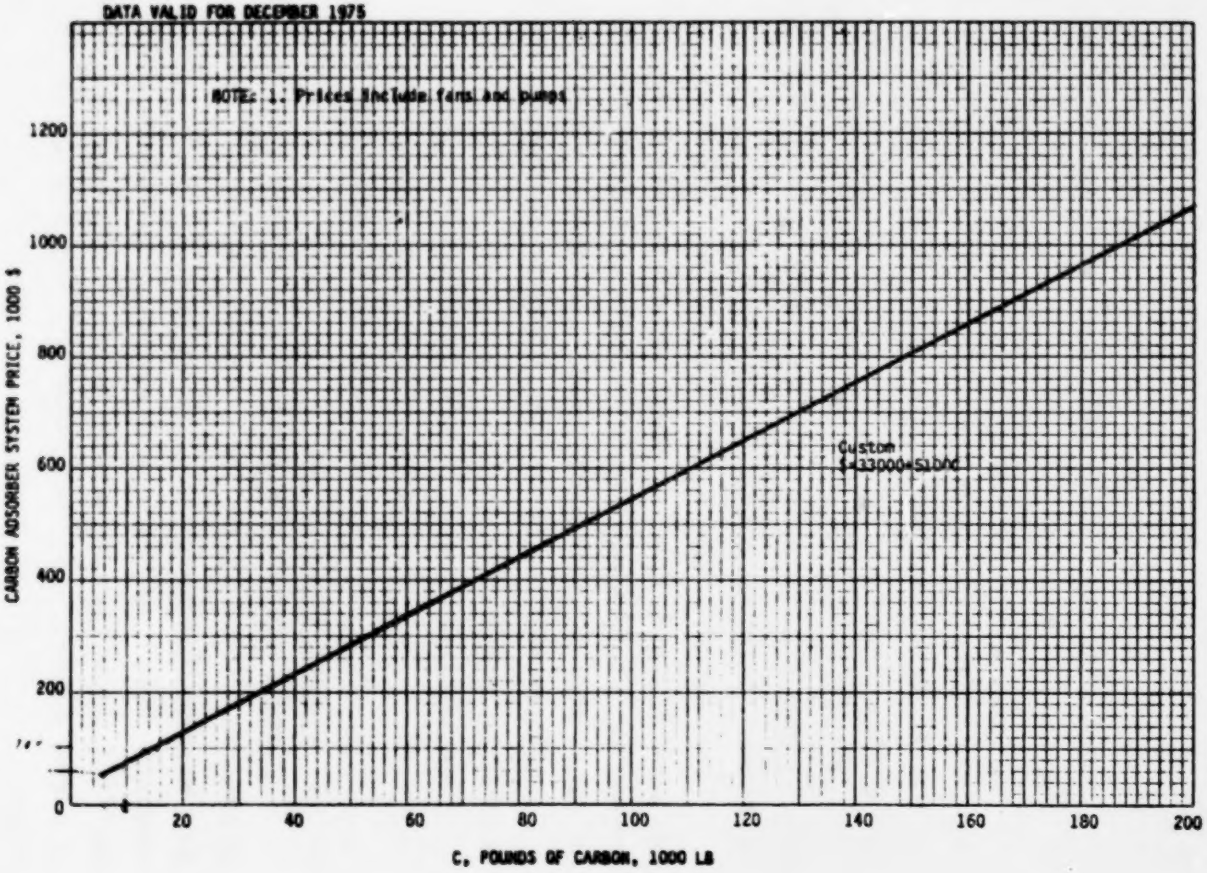


Figure 5-9. Carbon adsorption capital costs.[80]

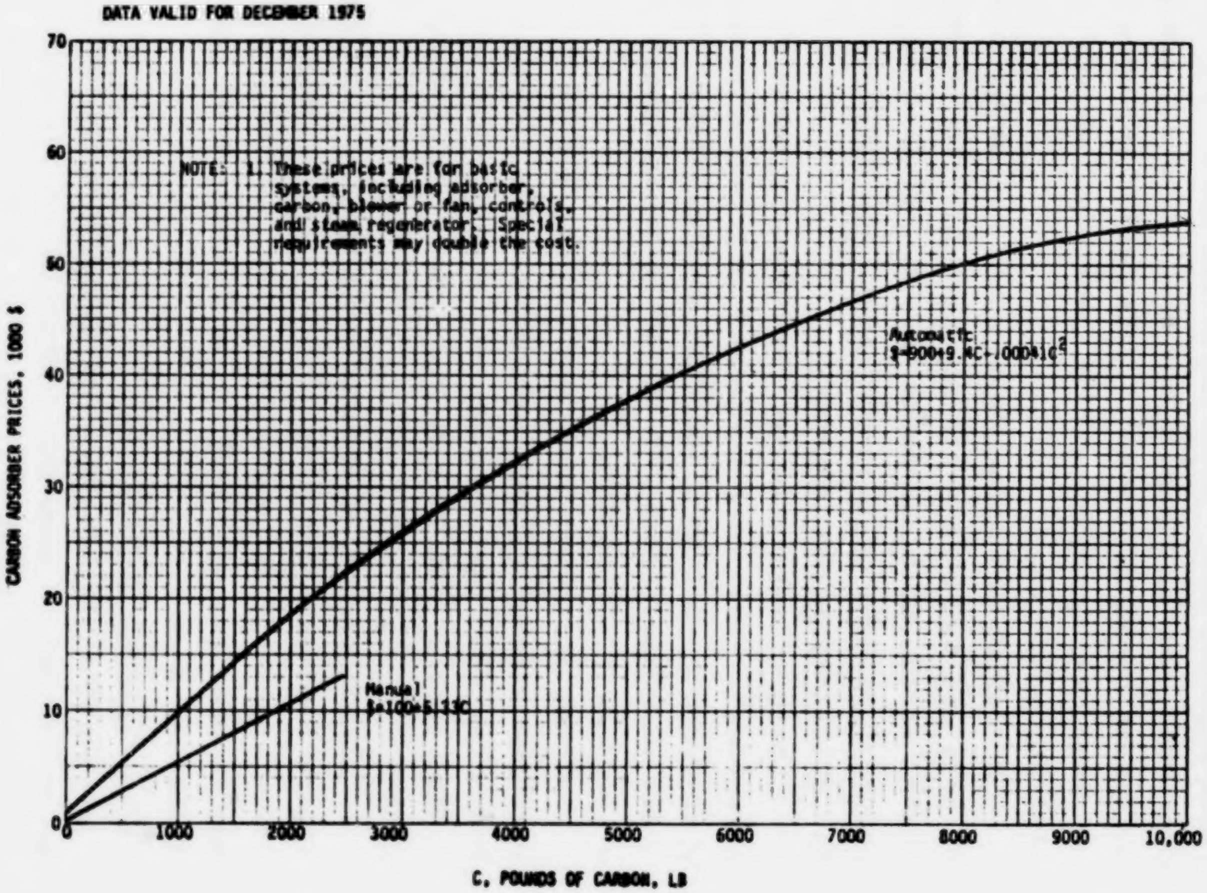


Figure 5-10. Carbon adsorption capital costs - small units.[80]

steam regenerators. Total installed costs (not including duct work, stack, and hooding) are 1.8 to 2.6 times the equipment purchase price.[80] This factor includes engineering, tax, freight, and contingencies, as well as installation costs.

Operating and maintenance costs are shown as a function of acfm and ppm benzene in Figure 5-11. The annualized costs, including fixed costs, may be obtained by adding about 15 percent of the total installed cost.

### 5.3.3 Catalytic Incinerators

Costs of catalytic incinerators are based on volumetric throughput. Heat exchangers may be provided to save on energy costs, but they increase capital costs. Figure 5-12 shows purchase prices for catalytic incinerators with and without heat exchangers.

Total installed costs are usually 1.8 to 2.6 times the purchase price.[80] They include not only direct installation costs but also tax, freight, engineering, and contingency costs; they do not include duct work, fan, stack, or hooding costs.

Annual operating and maintenance costs are given in Figure 5-13 as a function of flow rate (acfm) and benzene concentration. The annualized cost, including fixed costs, may be obtained by adding about 15 percent of the total installed costs.

### 5.3.4 Thermal Incinerators

Thermal incinerators are designed to allow 0.3 to 0.6 second retention time for combustion of low concentrations of benzene. Figures 5-14 and 5-15 show purchase prices for thermal incinerators, with and without heat exchangers, as a function of acfm and retention time. Total installed costs (not including fan, duct work, stack, hooding, etc.) are about 1.8 to 2.6 times the purchase price.[3] These costs

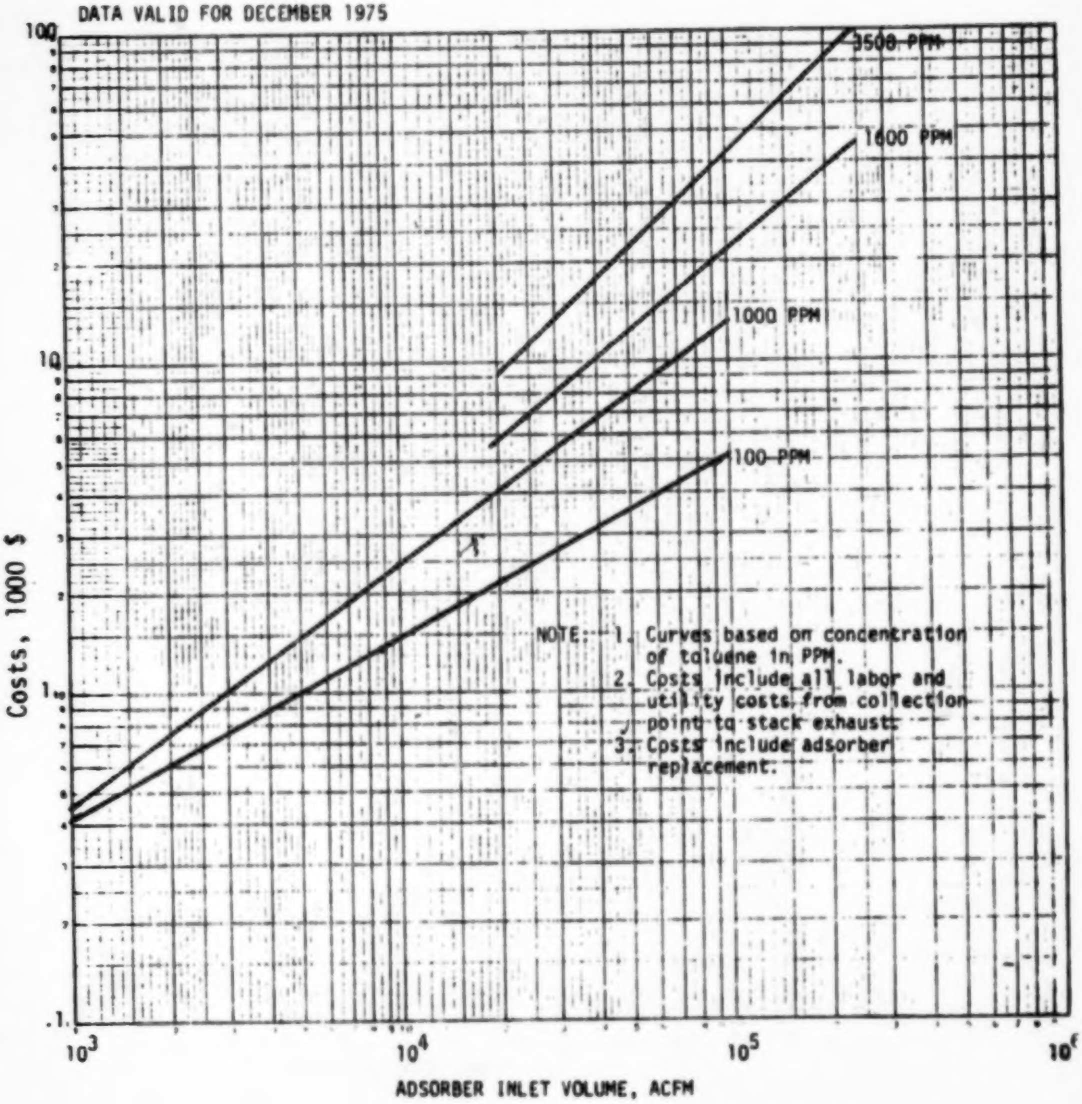


Figure 5-11. Carbon adsorption unit operating and maintenance cost vs. acfm and hydrocarbon concentration.[80]

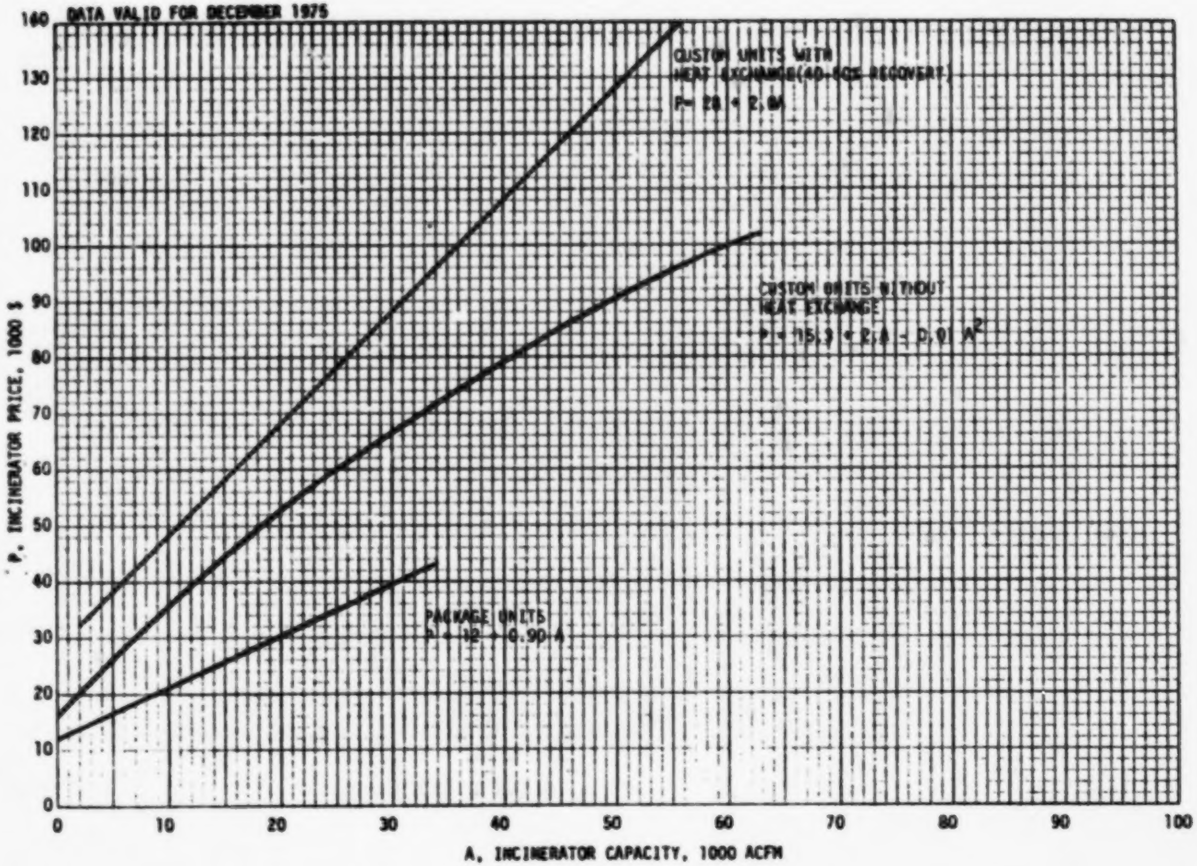
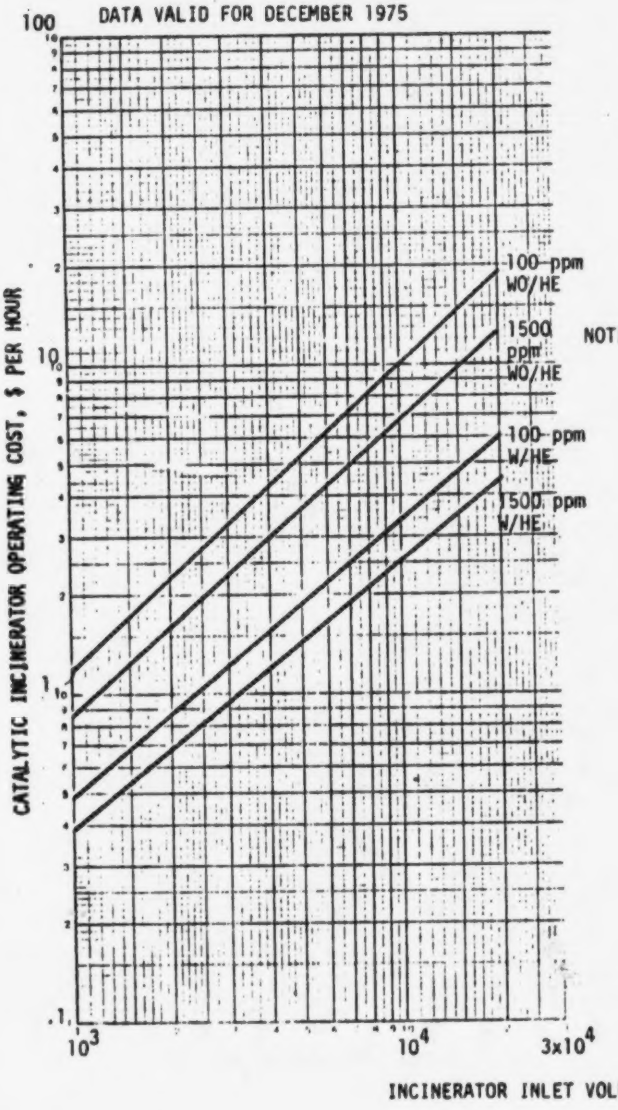


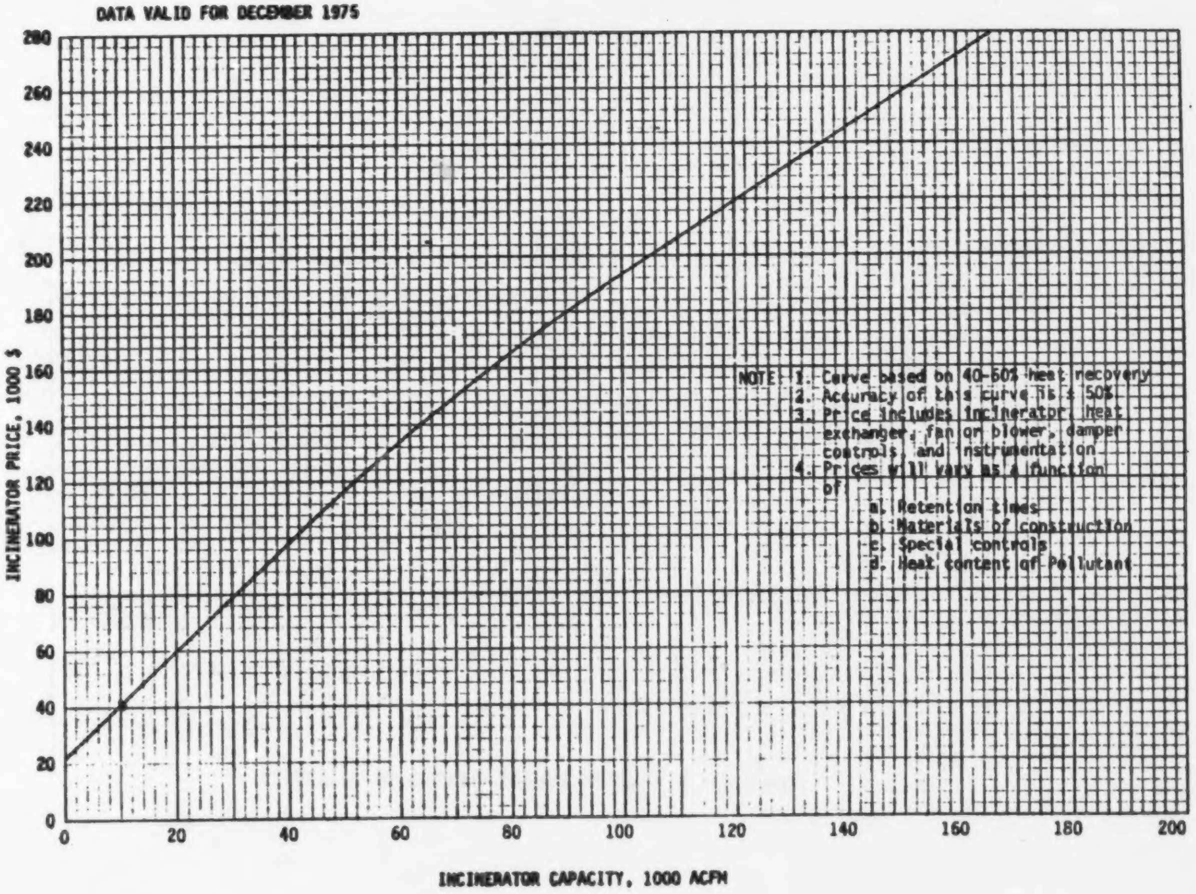
Figure 5-12. Catalytic incinerator prices.[80]



NOTE:
1. Curves based on ppm concentration of hydrocarbons such as toluene, ketones, and napthas.
2. Costs include all labor and utility costs from collection point to stack exhaust.
3. Cost include catalyst replacement.
4. Costs with and without heat exchangers included.

Figure 5-13. Catalytic incinerator operating and maintenance cost vs. acfm and hydrocarbon concentration.[80]

DATA VALID FOR DECEMBER 1975



NOTE: 1. Curve based on 40-60% heat recovery
2. Accuracy of this curve is ± 50%
3. Price includes incinerator, heat exchanger, fan or blower, damper controls, and instrumentation
4. Prices will vary as a function of
a. Retention times
b. Materials of construction
c. Special controls
d. Heat content of Pollutant

Figure 5-14. Prices for thermal incinerators with heat exchangers.[80]

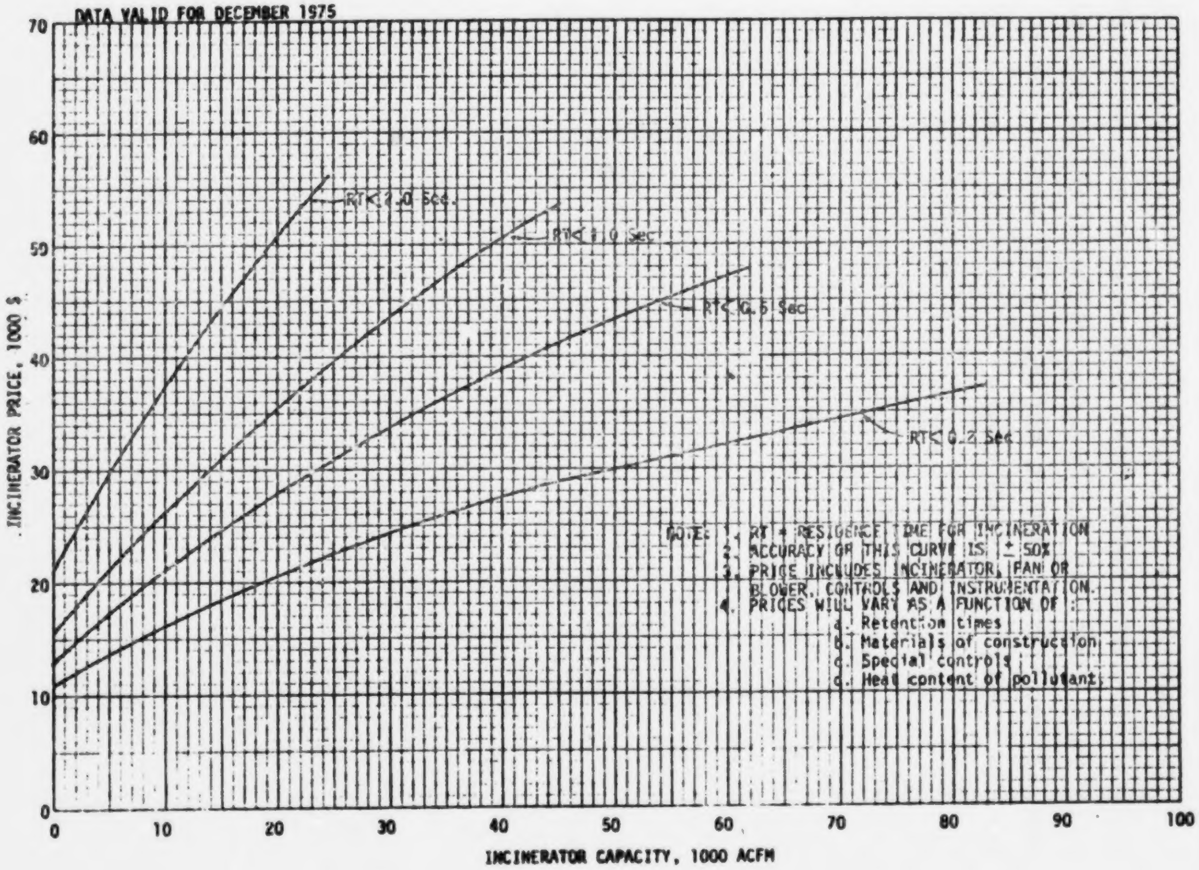


Figure 5-15. Prices for thermal incinerators without heat exchangers.[80]

include tax, freight, engineering, and contingencies, as well as direct installation costs.

Annual costs for operating and maintenance of incinerators with and without heat exchangers are shown in Figure 5-16 as a function of benzene concentration and flow rate. Annualized costs may be estimated by adding about 15 percent of the total installed costs to include fixed costs.

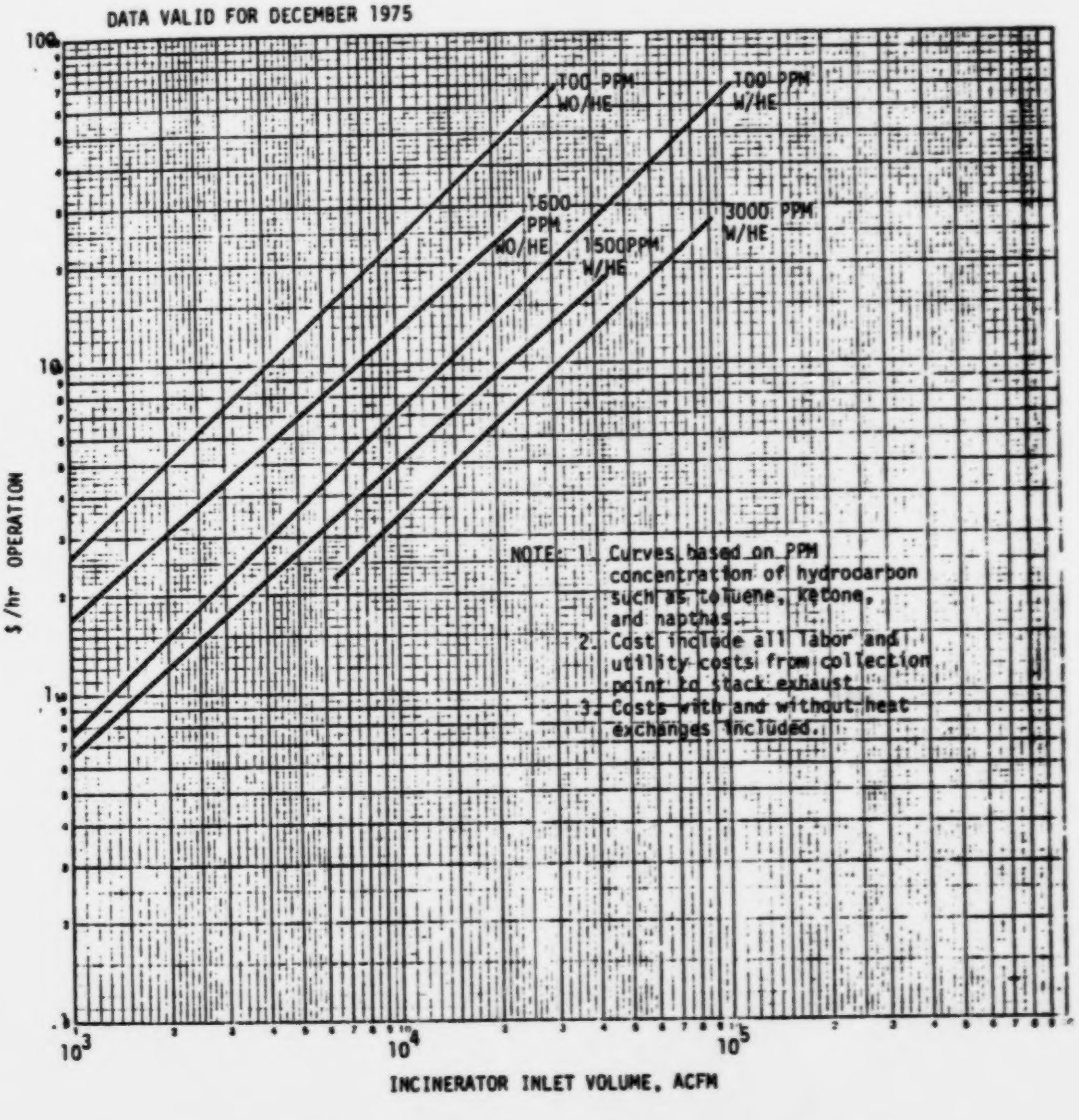


Figure 5-16. Thermal incinerator operating and maintenance cost vs. acfm and hydrocarbon concentration.[80]

# 6.0 EMISSION TRENDS

However they are calculated, emission predictions are always inexact. This is particularly true of benzene emission projections because of future uncertainties regarding the entire chemical market (especially benzene production industries) and gasoline consumption. Demand for benzene as a petrochemical has a direct bearing on its availability for blending into the gasoline pool. All these factors affect the type and quantity of projected benzene emissions. Total national benzene emissions are predicted to decrease by approximately 57 percent between 1976 and 1985, mostly as a result of reduced automobile emissions.

## 6.1 MOBILE SOURCE TRENDS

Available data indicate that gasoline-powered motor vehicles will remain the major source of benzene emissions nationally. They will be a less dominant source than at present, however, because 1985 auto emissions are projected to fall to about 24 percent of the 1976 level. This sharp decrease is predicated primarily on the assumption that nearly all cars will have catalyst control systems to meet the anticipated 0.41 g/mile HC regulation. It is assumed that such a standard will not be retroactive for older vehicles; therefore, AP-42 data, which incorporate the effect of catalyst deterioration, are utilized in the trend projections.[31] Evaporative losses presented by AP-42 for the post-1979 period are greatly reduced to reflect the assumption that better control will be available to meet the more stringent overall standards.[31] Table 6-1 summarizes the estimates of 1985 benzene emissions from gasoline- and diesel-fueled motor vehicles.

Table 6-1. SUMMARY OF PROJECTED BENZENE EMISSIONS FROM MOBILE SOURCES IN 1985

| Source | Benzene emissions, Gg |
|---|---|
| Gasoline-powered motor vehicles | |
| Evaporative losses | 20.8 |
| Exhaust emission (catalyst) controlled | 27.8 |
| Total | 48.6 |
| Diesel-powered heavy-duty vehicles | |
| Evaporative losses | a |
| Exhaust emission | 1.6 |

[a] Not available.

### 6.1.1 Projected Emissions from Gasoline-Powered Motor Vehicles

Tighter emission controls are expected to reduce benzene emissions from both exhaust and evaporative sources. It is assumed that the benzene level of gasoline will remain at 2 percent by volume, the value utilized in the 1976 estimates, and that the benzene-to-HC ratio in exhaust will be 0.025, the level determined in recent exhaust tests.[52]

Projections of benzene emissions from gasoline-powered motor vehicles in 1985 are detailed in Table 6-2. All emission data are based on low-altitude, non-California cases. This projection assumes that both exhaust and

## Table 6-2. PROJECTED BENZENE EMISSIONS FROM GASOLINE-POWERED MOTOR VEHICLES IN 1985

| Vehicle model year | Age, years | a Fraction of miles traveled* | b Exhaust HC emissions, g/mi⁺ | c Evap. HC losses, g/mi§ |
|---|---|---|---|---|
| 1985 | 1 | 0.116 | 0.27 | 0.5 |
| 1984 | 2 | 0.135 | 0.32 | 0.5 |
| 1983 | 3 | 0.125 | 0.38 | 0.5 |
| 1982 | 4 | 0.122 | 0.43 | 0.5 |
| 1981 | 5 | 0.106 | 0.49 | 0.5 |
| 1980 | 6 | 0.086 | 0.54 | 0.5 |
| 1979 | 7 | 0.083 | 0.59 | 1.76 |
| 1978 | 8 | 0.072 | 0.65 | 1.76 |
| 1977 | 9 | 0.051 | 2.6 | 1.76 |
| 1976 | 10 | 0.037 | 2.8 | 1.76 |
| 1975 | 11 | 0.023 | 3.0 | 1.76 |
| 1974 | 12 plus | 0.045 | 6.2 | 1.76 |
| | | 1.000 | | |

Exhaust emission estimate = $(123 \times 10^6)^{\#}(9494)^{**}(0.025)\ \Sigma\ a \times b$
= $(123 \times 10^6)(0494)(0.025)(0.95)$
= 27.8 Gg/yr (61.3 million lb/yr)

Evaporative losses = $(123 \times 10^6)(9494)(0.020)\ \Sigma\ a \times c$
= $(123 \times 10^6)(9494)(0.020)(0.89)$
= 20.8 Gg/yr (45.9 million lb/yr)

Total 1985 benzene losses = 48.6 Gg/yr (107.2 million lb/yr)

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[*] AP-42, Supplement 5,[31] Table 3.1.2-5.

[+] AP-42, Supplement 5,[31] Table D.1-17, reference year 1985.

[§] Evaporative loss estimates from AP-42, Supplement 5,[31] Table D.1-27.

[#] National vehicle population projection data from DOT and the Motor Vehicle Manufacturers Association.

[**] Average annual miles traveled per vehicle in 1974.[95]

evaporative emission control technology available by about 1980 will control benzene emissions more effectively than the best available control technology in 1976. A more conservative projection of 1985 emissions can be developed by assuming that the best control technology as of 1976 will be used in 1985. Thus, the 1985 projection for exhaust emissions for the years 1978 to 1985 vehicles is altered to include the Olson data of 0.016 g/mile for new catalytically controlled vehicles[52] and a 1976-level evaporative loss rate of 1.24 g/mile for 1980 to 1985 vehicles.[30] A catalyst deterioration rate of 10 percent per year is also incorporated. The resulting exhaust emissions are 38.7 Gg/yr (85.3 million lb/yr) and evaporative losses are 32.7 Gg/yr (72.1 million lb/yr), giving a total emission rate of 71.4 Gg/yr (157.4 million lb/yr).

Over 95 percent of all 1975 and later model automobiles now have catalyst exhaust controls; a limited few have 'lean-burn' engines, and even fewer have thermal-reactor (stratified-charge) systems for hydrocarbon control.[165] To meet the more stingent hydrocarbon emission standards anticipated by 1985, all gasoline vehicles must employ some type of catalytic system. Since benzene emission is a function of its constituent level in the gasoline, any increase or decrease in blending affects exhaust-pipe benzene levels. Concentrations in gasoline are dependent on all of the following factors, which vary among refineries (i.e., the major benzene source) and with seasonal blends:

- Benzene content of the crude oil
- Operating characteristics of catalytic reformers
- The extent to which catalytic reformate is used as a blending component

- Use of benzene for petrochemicals and the resulting volume available for the gasoline pool.

Published projections indicate that even though the volume of crude oil processed in 1985 probably will be about 9 percent greater than in 1976, total gasoline production will decrease some 5 percent (to 100 billion gallons).[154] Conversely, the quantity of refinery benzene withdrawn for use as a chemical intermediate is expected to increase substantially. Energy and Environmental Analysis, Inc., (EEA) applies a value of roughly 1 percent benzene in gasoline blends (markedly lower than Short's 2 percent) and projects that 1985 gasoline blends will not exceed 2 percent.[154] EEA stipulates that this estimate involves a degree of uncertainty and that although the aromatic content of gasoline is likely to increase, the toluene and xylene levels will probably increase more than the benzene level. Both of these available constituents are higher volume gasoline constituents and have higher octane numbers (although benzene is a desirable blending component because of its volatility and other performance characteristics). Also, neither toluene nor xylene is as much in demand as benzene as a feedstock for petrochemical production.

### 6.1.2 Projected Emissions From Other Mobile Sources

Benzene emissions from diesel-powered motor vehicles are predicted to decrease 8 percent between 1976 and 1985, primarily because of an estimated decline in diesel fuel usage consistent with that of gasoline. This projection assumes no variance from the emission calculation given in Section 4.1.3 other than a decrease in diesel consumption from 9.6 billion to 9.2 billion gallons over the 9-year period. The fuel decline is based on the projected decline in 1985 gasoline production and on the assumption that the diesel fraction of the market remains constant.[154] This decline may not be wholly realistic in view of the control methods available to meet the more stringent hydrocarbon standards of the future, once promulgated. If the use of light-duty diesel vehicles offers a convenient means of meeting the lower emission limitations, their use may increase.

Because of the scarcity of information regarding benzene emissions from aircraft and other mobile sources, it is impossible to make a realistic projection of 1985 emissions.

## 6.2 STATIONARY SOURCE TRENDS

As discussed in Section 4.2, the primary stationary sources of atmospheric benzene emissions include the production of the compound, its use as a chemical intermediate, and the storage and distribution of benzene and gasoline. The portions of stationary-source benzene emissions contributed by these three major sources in 1976 are approximately 14, 64, and 22 percent, respectively. Projected 1985 distribution figures (14, 68, and 18 percent) do not differ significantly despite the anticipated 30 percent increase in stationary sources of benzene emissions between 1976 and 1985.

### 6.2.1 Benzene Production

Although less atmospheric benzene is generated and lost during benzene production than from other stationary sources, the volume is still significant. Manufacture of benzene as a by-product of coke-oven operations represents a relatively minor portion of total benzene production, but it is a significant source of localized atmospheric benzene because of the poor vapor containment within the typical oven battery. Although emissions from coking operations are projected to increase approximately 20 percent by 1985, improved coke-oven battery emission controls could reduce these emissions to well below 1976 levels. Benzene emissions from refineries are projected to increase approximately 42 percent by 1985, primarily because of the expected increase in benzene production volume.

### 6.2.2 Benzene Consumption Processes

As the result of a predicted growth rate of 6 percent per year between 1976 and 1985, demand for benzene as a chemical intermediate is expected to be about 2.4 billion gallons per year by 1985.[11] The 1976 benzene demand for consumption processes was only about 1.5 billion gallons.[154] This increase in volume of consumption is expected to cause a 39 percent increase in benzene emissions by 1985. Projected benzene emissions are based on 1976 emission factors and estimated 1985 production rates.

#### Nitrobenzene (Aniline)

Nitrobenzene is prepared by direct nitration of benzene using mixed nitric and sulfuric acids. Generally, about 85 percent of the chemical is used in the manufacture of aniline. The demand for aniline corresponds directly to the demand for a wide variety of plastics, synthetic fibers, rubber chemicals, drugs, and dyes in which it is used. Domestic nitrobenzene production capacity in 1975 was approximately 1.07 billion pounds.[55] Benzene emissions from nitrobenzene manufacture are projected for 1985. Figure 6-1 correlates the future demand upon benzene supply with increased aniline production. Because of the lack of documented data on atmospheric benzene emission from aniline manufacture, future levels are not projected.

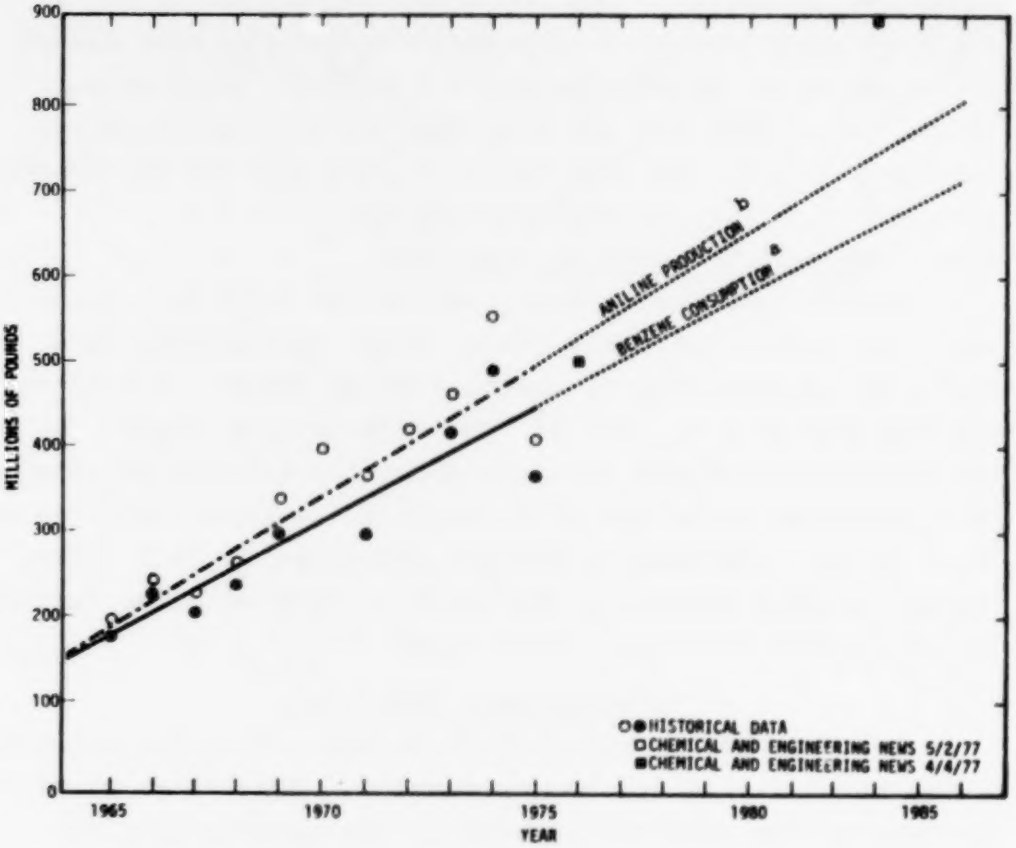

Figure 6-1. Historical and projected domestic aniline production and corresponding benzene consumption.

[a] Linear regression for the consumption of benzene was developed from 10 year historical data (1965-1975).

[b] Linear regression for chemical production developed from 10 year historical data (1965-1975).

## Ethylbenzene (Styrene)

Production of ethylbenzene, primarily from the alkylation of benzene with ethylene, has been the principal consumer of domestic benzene. As early as 1965, ethylbenzene manufacture consumed 41 percent of the entire domestic benzene production. Over 90 percent of the ethylbenzene produced in the United States today is used for the manufacture of styrene and its derivatives. Present domestic styrene capacity greatly outweighs demand, and no change in this situation is predicted through 1980. Ethylbenzene/styrene demand should continue to increase at the present rate of 6 to 7 percent annually until 1980, after which a decrease to 5 percent annually is predicted.[101] It is anticipated that ethylbenzene and its styrene derivatives will use approximately 50 percent of the domestic benzene produced in 1985. Figure 6-2 presents projected demands on benzene supply based on the increase in ethylbenzene/styrene production. The 1985 benzene emissions from processing both of these compounds are expected to increase some 90 percent over 1976 estimates.

## Maleic Anhydride

Of the present domestic maleic anhydride supply, 81.3 percent is produced from benzene oxidation, 16.7 percent is derived from butanes, and the remaining 2 percent is a phthalic anhydride by-product. Figure 6-3 relates future demands on benzene supply to the projected increase in maleic anhydride production. Nearly half of all the atmospheric benzene emitted from the petrochemical category results from the manufacture of maleic anhydride. The projected 1985 increase in benzene emissions from this source is approximately 14 percent.

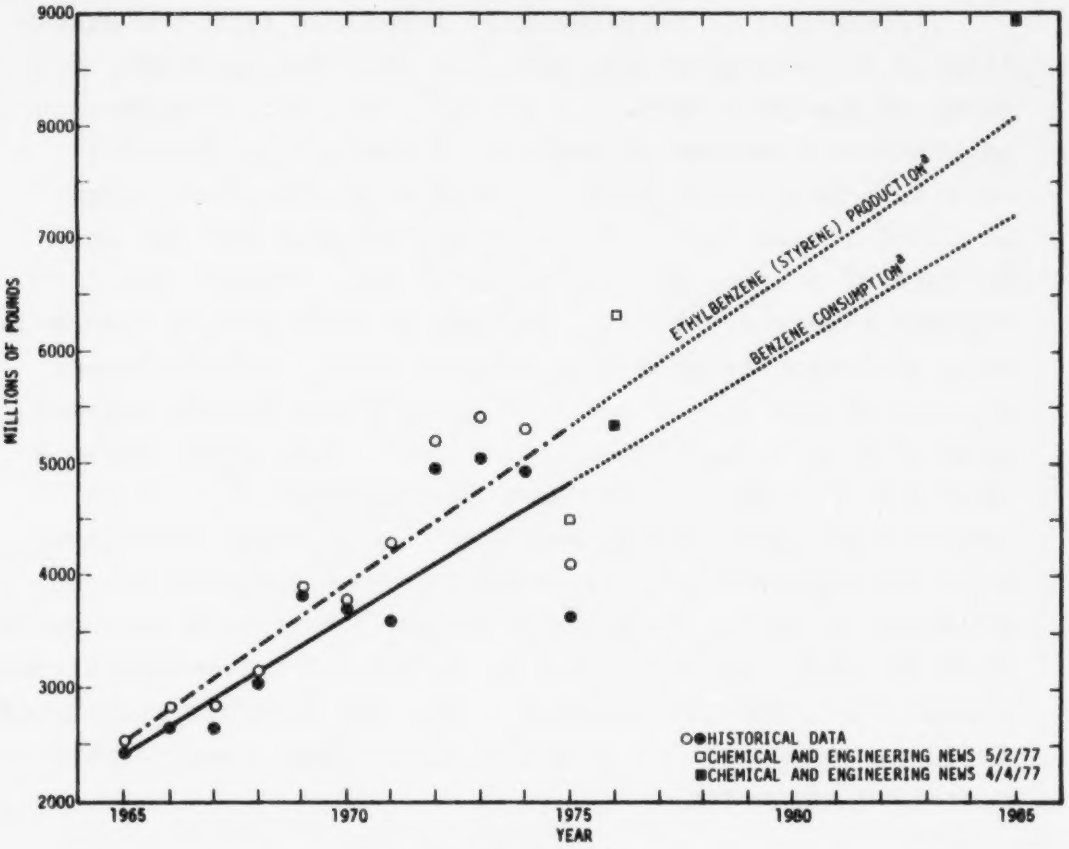

Figure 6-2. Historical and projected domestic ethlylbenzene production and corresponding benzene consumption.

[a] Linear regression for the consumption of benzene and the production of ethylbenzene were developed from 10 year historical data (1965-1975).

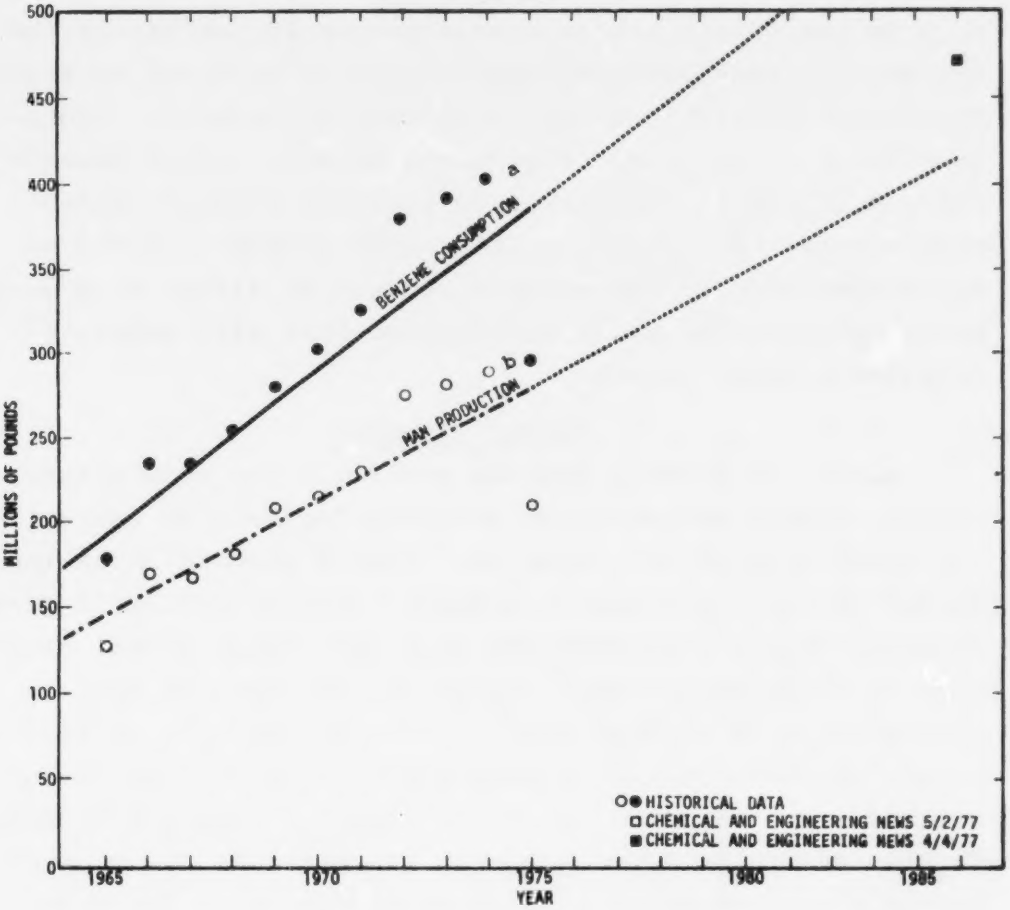

Figure 6-3. Historical and projected domestic maleic anhydride production and corresponding benzene consumption.

[a] Linear regression for the consumption of benzene was developed from 10 year historical data (1965-1975).

[b] Linear regression for chemical production developed from 10 year historical data (1965-1975).

## Cyclohexane

In the United States approximately 25 percent of the cyclohexane manufactured commercially is produced by fractionation of petroleum and 75 percent by catalytic hydrogeneration of benzene. Figure 6-4 relates future demands on benzene supply to the projected increase in cyclohexane manufacture. Although the literature search produced no documented data on atmospheric benzene emissions from cyclohexane production, it is anticipated this will remain a relatively minor source.

## Phenol (Cumene)

Among the several methods available for manufacture of phenol, cumene peroxidation accounts for over 90 percent of the total U.S. phenol capacity. Phenol production is the second largest consumer of benzene. Approximately 20 percent of total domestic benzene was used for cumene/phenol production in 1965; the present figure is the same and is predicted to apply through 1985. Since future U.S. benzene supply is not expected to meet phenol demand, more phenol will be imported from foreign producers. Figure 6-5 depicts future demands on benzene supply in correlation with projected increases in cumene/phenol production. Based on these projections, benzene emissions from phenol production in 1985 will be about 50 percent higher than the 1976 volume unless abatement procedures are improved. Similarly, projected 1985 benzene emissions from the manufacture of cumene are proportionately higher.

## Chlorobenzenes

The annual benzene emission level attributed to the manufacture of chlorobenzenes, as determined by Monsanto, is approximately 2.29 Gg.[66] Emissions are projected to increase nearly 40 percent by 1985.

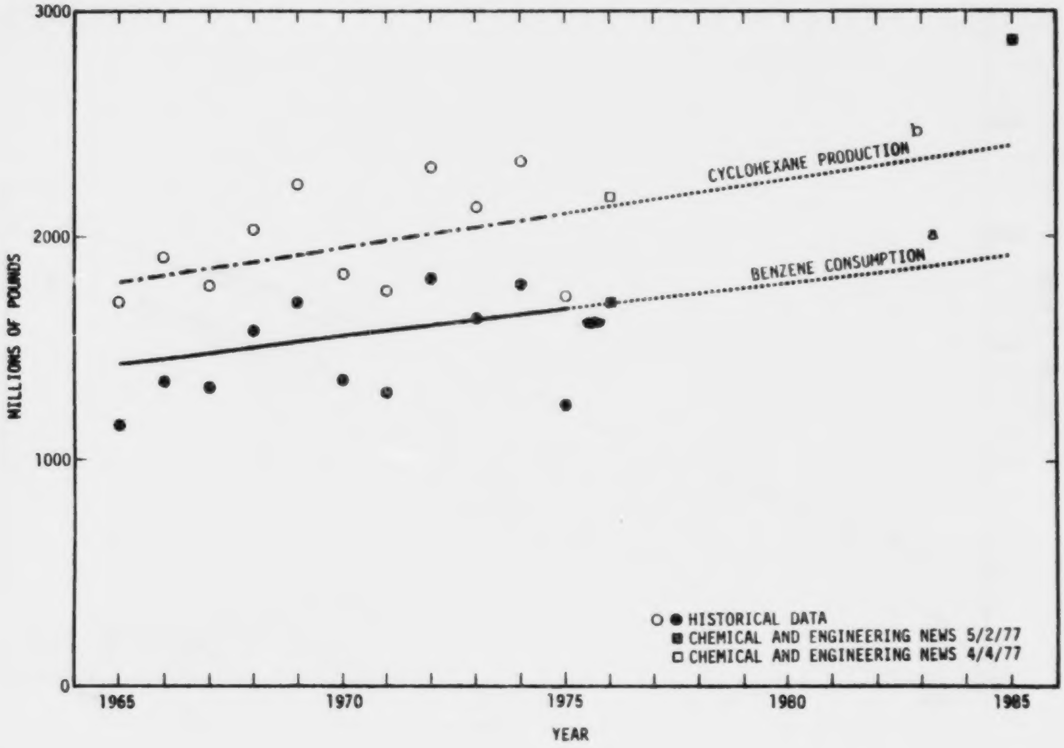

Figure 6-4. Historical and projected domestic cyclohexane production and corresponding benzene consumption.

[a] Linear regression for the consumption of benzene was developed from 10 year historical data (1965-1975).

[b] Linear regression for chemical production developed from 10 year historical data (1965-1975).

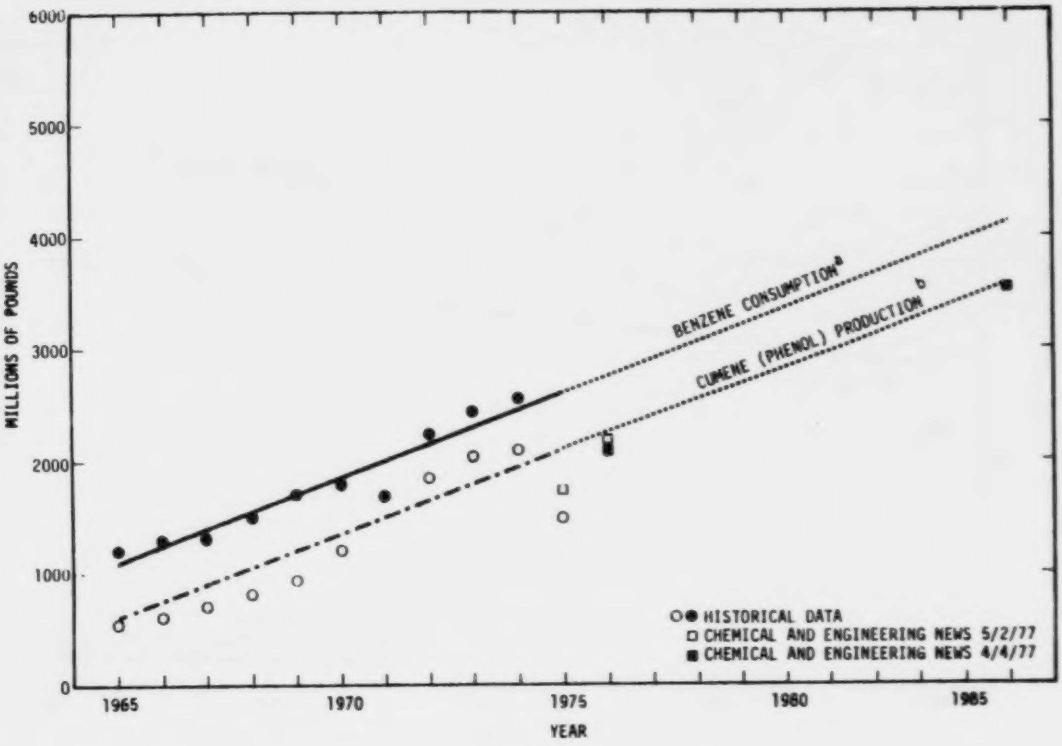

Figure 6-5. Historical and projected domestic cumene (phenol) production and corresponding benzene consumption.

[a] Linear regression for the consumption of benzene was developed from 10 year historical data (1965-1975).

[b] Linear regression for chemical production developed from 10 year historical data (1965-1975).

### Detergent alkylate

As stated in Section 4.2.3, detergent alkylate, is the name commonly given to a product formed from the catalytic alkylation of benzene with dodecene. The product made may be either branched or linear alkylbenzene (dodecylbenzene). Benzene emission data are obtainable only for the latter production, and these were used to project a 1985 emission increase of approximatly 36 percent, or 0.19 Gg total. This estimate could be low.

### Solvent operations

Benzene has a wide range of applications as an industrial solvent but is being replaced by less toxic products. Although no benzene emission data are available on which to base projected future atmospheric levels, solvents could remain an important emission source. The benzene contaminant level in other solvents may be a major determinant in estimating the total solvent emissions.

### Other nonfuel uses

Additional nonfuel uses of benzene that are regarded as potential emission sources include the production of fumaric acid, cumene sulfonate ammonium salt, cumene sulfonic acid, benzonitrile, and anthraquinone. The increase in benzene emissions from the manufacture of these chemicals is projected to be approximately 40 percent by 1985. This figure depends on the volume of benzene production and consumption.

## 6.2.3 Storage and Transport Emissions

Although storage and distribution of gasoline and benzene (including "feedstock" benzene stored by noncaptive consumer industries as described in Section 4.2.3) are significant sources of benzene emissions, they are expected to increase only slightly in overall volume (approximately

2.5 percent) by 1985. It is assumed that little or no benzene is emitted in the storage and transport of consumer chemicals (ethylbenzene, cumene, cyclohexane, etc.) for which benzene is a raw material; therefore, this source is not considered in the projection. Any projected increase in benzene emissions from storage and transport systems is offset considerably by the decline in the total gasoline supply predicted for 1985. More effective vapor control methodology is also anticipated. Combined benzene emissions from gasoline storage and distribution and those from service station operations are predicted to be lower by some 5 percent than 1976 levels. General population exposure from service station operations will remain significant. The increasing number of self-service operations make this potentially the largest exposure source by 1985. Emissions from the storage and transport of product benzene are predicted to increase significantly (approximately 65 percent) because of the projected increase in production volume by 1985. As stated above, this increase is offset by the estimated decrease in benzene emissions from gasoline storage/distribution.

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# APPENDIX A

# APPENDIX A

Data from three automobile exhaust emission studies are presented. Table A-1 gives emissions data from the Black and Bradow study;[17] Table A-2 gives emission test data from Olson Laboratories.[52] A Bureau of Mines auto emissions study[4] is described, and relevant test data are presented.

## BUREAU OF MINES STUDY[4] OF THE EFFECT OF AUTOMOBILE OPERATING VARIABLES ON EXHAUST EMISSIONS

Six 1970-1972 vehicles were tested in a 1973 study. Results of this test are listed in Table A-3.[4] These vehicles were equipped with the following emission-control systems:

- A base-metal oxidation catalyst system with exhaust gas recirculation (EGR)
- An Esso rapid-action manifold (RAM) thermal reactor system with EGR
- Two systems with platinum oxidation catalyst and EGR
- An Ethyl lean-reactor system with EGR
- An Esso dual-catalyst system (Monel reduction catalyst and platinum oxidation catalyst).

The experimental program revealed two areas of interest: first, the influence of fuel composition on exhaust hydrocarbon emission and constituent benzene content; second, the effect of temperature variation (simulating seasonal conditions) on benzene emissions. In the fuel composition phase of the study, all six vehicles were operated on high-aromatic

## Table A-1. TOTAL HYDROCARBON AND BENZENE EMISSIONS FROM TEN 1975 AUTOMOBILES[17]

| Vehicle | FIA[a] hydrocarbons,[c] g/mile[d] | GC[b] total hydrocarbons, g/mile[d] | GC[b] benzene, g/mile[d] |
|---|---|---|---|
| 1972 Chevrolet | 1.00±0.19 (3.00) | 1.150±0.11 | 0.029 |
| 1975 Ford Prototype | 0.307±0.082 (0.41) | 0.214±0.034 | 0.008 |
| 1975 Olds. Prototype | 0.436±0.051 (1.50) | 0.485+0.073 | e |
| 1975 Ply. Prototype | 0.242±0.017 (0.41) | 0.257±0.044 | 0.008 |
| 1975 Chev. Impala | 0.279±0.060 (1.50) | 0.249±0.044 | 0.004 |
| 1975 Chev. Nova | 0.291±0.030 (1.50) | 0.264±0.048 | 0.003 |
| 1975 Ply. Fury | 0.560±0.120 (1.50) | 0.488±0.074 | 0.010 |
| 1975 Ply. Scamp | 0.731±0.130 (1.50) | 0.658±0.026 | 0.015 |
| 1975 Ford Granada | 0.581±0.115 (1.50) | 0.550±0.041 | 0.004 |
| 1975 Ford Torino | 0.950±0.091 (1.50) | 0.788±0.034 | 0.015 |

[a] Measurements determined by flame ionization analyzer (FIA).

[b] Measurements determined by gas chromatograph (GC).

[c] Numbers in parentheses indicate applicable emission standard.

[d] Multiply by 0.621 for conversion to g/km.

[e] Data not reported.

## Table A-2. HYDROCARBON AND BENZENE EMISSION DATA FROM OLSON LABORATORIES TESTING PROGRAM (1975 CALIFORNIA VEHICLES)[52]

| Vehicle No. | Make | Model | CID | Hydro-carbon g/mile | Benzene, g/mile | Benzene hydrocarbon, % |
|---|---|---|---|---|---|---|
| 1 | Chev | G10V | 350 | 0.48 | 0.007 | 1.4 |
| 2 | Chev | Scout | 350 | 0.66 | 0.016 | 2.4 |
| 3 | Chev | G10V | 350 | 1.08 | 0.020 | 1.8 |
| 4 | Chev | G10V | 350 | 0.74 | 0.010 | 1.4 |
| 5 | Dodge | TRAD | 318 | 0.67 | 0.022 | 3.3 |
| 6 | Ford | F100 | 300 | 0.68 | 0.021 | 3.1 |
| 7 | Ford | F100 | 302 | 2.43 | 0.108 | 4.4 |
| 8 | Ford | Econ | 351 | 0.56 | 0.016 | 2.8 |
| 9 | Ford | F100 | 351 | 0.72 | 0.010 | 1.4 |
| 10 | GMC | Sier | 350 | 1.38 | 0.028 | 2.0 |
| 11 | AMC | Pacer | 258 | 0.35 | 0.012 | 3.4 |
| 12 | Buick | Cnty | 350 | 0.89 | 0.054 | 6.1 |
| 13 | Buick | Esta | 455 | 0.54 | 0.018 | 3.3 |
| 14 | Buick | Regal | 350 | 0.38 | 0.010 | 2.6 |
| 15 | Cadi | Devi | 500 | 0.77 | 0.015 | 1.9 |
| 16 | Chev | Monz | 140 | 0.30 | 0.007 | 2.3 |
| 17 | Chev | Came | 250 | 0.49 | 0.010 | 2.0 |
| 18 | Chev | Mont | 350 | 0.51 | 0.007 | 1.4 |
| 19 | Chev | Came | 350 | 0.86 | 0.023 | 2.7 |
| 20 | Chev | Mont | 350 | 0.62 | 0.010 | 1.6 |
| 21 | Chev | Impa | 400 | 0.44 | 0.007 | 1.6 |
| 22 | Chry | Newp | 400 | 0.44 | 0.011 | 2.5 |
| 23 | Dodge | Dart | 318 | 0.22 | 0.007 | 3.2 |
| 24 | Dodge | Dart | 225 | 0.38 | 0.005 | 1.3 |
| 25 | Ford | Must | 140 | 0.12 | 0.003 | 2.5 |
| 26 | Ford | Gran | 302 | 0.78 | 0.012 | 1.5 |
| 27 | Ford | Gran | 250 | 0.33 | 0.008 | 2.4 |
| 28 | Ford | Tori | 351 | 0.57 | 0.011 | 1.9 |
| 29 | Ford | LTD | 460 | 0.64 | 0.012 | 1.9 |
| 30 | Merc | Marq | 400 | 0.46 | 0.023 | 5.0 |
| 31 | Merc | Coug | 351 | 0.38 | 0.009 | 2.4 |
| 32 | Olds | Cutl | 350 | 0.74 | 0.047 | 6.4 |
| 33 | Olds | Cutl | 350 | 0.38 | 0.008 | 2.1 |
| 34 | Olds | Delta | 455 | 0.57 | 0.007 | 1.2 |
| 35 | Plym | Fury | 318 | 0.77 | 0.014 | 1.8 |
| 36 | Plym | Dust | 225 | 0.24 | 0.004 | 1.7 |
| 37 | Pont | Cata | 400 | 0.61 | 0.009 | 1.5 |
| 38 | Pont | Vent | 350 | 0.30 | 0.008 | 2.7 |
| 39 | Pont | Grnv | 455 | 0.41 | 0.009 | 2.2 |
| 40 | Capri | II | 140 | 1.44 | 0.038 | 2.6 |
| 41 | Dats | B210 | 85 | 0.34 | 0.010 | 2.9 |
| 42 | Hond | CVCC | 91 | 0.74 | 0.018 | 2.4 |
| 43 | Toyo | Coro | 133 | 0.15 | 0.003 | 2.0 |
| 44 | VW | Seda | 97 | 0.51 | 0.009 | 1.8 |
| 45 | VW | Rabb | 90 | 0.32 | 0.008 | 2.5 |
|  |  |  |  | $\bar{x}$ = 0.61 | 0.016 | 2.5 |
|  |  |  |  | $\sigma$ = 0.39 | 0.018 |  |

## Table A-3. INFLUENCE OF FUEL COMPOSITION ON TOTAL HYDROCARBON EMISSION AND CONSTITUENT BENZENE IN EXHAUST FROM PROTOTYPE LOW EMISSION VEHICLES[4]

| Fuel | Total[a] HC emissions, g/mile | Total[a] HC emissions, g/km | Benzene emission[a] Total HC wt. pct | Benzene emission[a] g/mile | Benzene emission[a] mg/km |
|---|---|---|---|---|---|
| 1972 Oldsmobile Delta 88 (Car 403) With A 455-CID Engine And Equipped With A Base-Metal Oxidation Catalyst And EGR | | | | | |
| Typical clear I, 35 percent aromatic (7202) | 0.33 | .21 | 7.7 | 0.025 | 15 |
| Indolene clear, 22 percent aromatic (7203) | 0.43 | 0.27 | 6.0 | 0.026 | 16 |
| High alkylate, 10 percent aromatic (7212) | 0.50 | 0.31 | 2.9 | 0.015 | 9 |
| 1971 Ford LTD (Car 810) With A 351-CID Engine And Equipped With ESSO Ram Reactors And EGR | | | | | |
| Typical clear I, 35 percent aromatic (7202) | 0.17 | 0.11 | 4.5 | 0.008 | 5 |
| Indolene clear, 22 percent aromatic (7203) | 0.11 | 0.07 | 4.3 | 0.005 | 3 |
| High alkylate, 10 percent aromatic (7212) | 0.13 | 0.08 | 1.8 | 0.002 | 1 |
| 1971 Plymouth Fury III (Car 333) With A 360-CID Engine And Equipped With Platinum Oxidation Catalysts And EGR | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 0.40 | 0.25 | 5.8 | 0.023 | 14 |
| Indolene clear, 22 percent aromatic (7203) | 0.39 | 0.24 | 3.9 | 0.015 | 9 |

(Continued)

Table A-3 (continued).

| Fuel | Total[a] HC emissions, g/mile | Total[a] HC emissions, g/km | Benzene emission[a] Total HC wt. pct | Benzene emission[a] g/mile | Benzene emission[a] mg/km |
|---|---|---|---|---|---|
| High alkylate, 10 percent aromatic (7212) | 0.50 | 0.31 | 1.5 | 0.008 | 5 |
| 1972 Ford Torino (Car 724) With A 351-CID Engine And Equipped With Platinum Oxidation Catalysts And EGR | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 0.72 | 0.45 | 4.2 | 0.030 | 19 |
| Indolene clear, 22 percent aromatic (7203) | 0.79 | 0.49 | 3.2 | 0.025 | 15 |
| High alkylate, 10 percent aromatic (7212) | 0.86 | 0.53 | 1.3 | 0.011 | 7 |
| 1971 Plymouth Fury III (Car 775) With A 360-CID Engine And Equipped With The Ethyl Lean Reactors And EGR | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 0.43 | 0.27 | 5.0 | 0.022 | 14 |
| Indolene clear, 22 percent aromatic (7203) | 0.44 | 0.27 | 3.5 | 0.015 | 9 |
| High Alkylate, 10 percent aromatic (7212) | 0.36 | 0.22 | 1.7 | 0.006 | 4 |

(Continued)

Table A-3 (continued).

| Fuel | Total[a] HC emissions, | | Benzene emission[a] | | |
|---|---|---|---|---|---|
| | g/mile | g/km | Total HC wt. pct | g/mile | mg/km |
| 1970 Chevrolet Impala (Car 58) With A 350-CID Engine And Equipped With GEM Monel $NO_x$ Reduction Catalysts And Platinum Oxidation Catalysts | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 0.30 | 0.19 | 3.7 | 0.011 | 7 |
| Indolene clear, 22 percent aromatic (7203) | 0.34 | 0.21 | 2.5 | 0.009 | 6 |
| High alkylate, 10 percent aromatic (7212) | 0.40 | 0.25 | 1.1 | 0.004 | 2 |

[a] All tests were conducted at 24°C ambient temperature. Data are weighted in accordance with the 1975 Federal test procedure and each value represents the average of three replicate tests.

(up to 40%), midrange-aromatic (21 to 22%), and low-aromatic (8 to 10%) fuels. Table A-4 lists the fuel characteristics. Five of the vehicles showed a decrease in benzene emission with the decrease in fuel aromaticity. Three showed an increase in hydrocarbon emission with decreasing fuel aromaticity.* The remaining vehicles showed few conclusive effects attributable to fuel composition.

In the temperature-variation phase of the study only three of the six vehicles were used in tests at ambient temperatures of -4, 7, 24, and 35°C. Test procedures and fuels were the same as in the earlier tests. Table A-5 lists the test vehicles and the data collected. The data show that total hydrocarbon emissions were lowest at 24°C and increased when the ambient temperature was either higher or lower than 24°C. Generally, the same trend was apparent in benzene emissions in most of the tests. The increase in THC was much more pronounced when the temperature was decreased than when it was increased.

For comparison with tests of these prototype low-emission vehicles, an additional study on the influence of fuel composition was conducted with 10 production vehicles (1970-1973) that had no exhaust control devices.[4] Table A-6 lists these vehicles and the results of the study, which was conducted with the same fuels and testing procedures used earlier. Results show that total hydrocarbon emissions from these uncontrolled vehicles were far higher than those from the controlled vehicles.

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* It should be noted that increases in fuel aromaticity result in increased fuel density, which can affect carburetor metering, which in turn can affect air/fuel ratio. Therefore, THC emissions may be influenced by changes in air/fuel ratio rather than changes in fuel aromaticity.

Table A-4. FUEL DATA[4]

| | Typical clear I (7202) | Typical clear II (7221) | Indolene clear (7203) | High alkylate (7212) |
|---|---|---|---|---|
| Reid vapor pressure. . . . . | 8.8 | 9.1 | 9.0 | 9.1 |
| Specific gravity . . . . . . | .745 | .755 | .720 | .704 |
| API gravity. . . . . . . . . | 58.4 | 55.7 | 65.0 | 69.5 |
| Octane number, research method. . . . . . . . . . . | 91 | 93 | 91 | 94 |
| Distillation, °C | | | | |
| IBP . . . . . . . . . . | 34 | 36 | | 34 |
| 10 pct evaporated . . . | 56 | 58 | 53 | 58 |
| 50 pct evaporated . . . | 105 | 107 | 96 | 101 |
| 90 pct evaporated . . . | 163 | 161 | 150 | 147 |
| End point . . . . . . . | 202 | 199 | 189 | 197 |
| Composition, vol pct (FIA) | | | | |
| Aromatics . . . . . . . | 33 | 39 | 21 | 8 |
| Olefins . . . . . . . . | 9 | 8 | 10 | 8 |
| Paraffins . . . . . . . | 58 | 53 | 69 | 84 |
| Composition, vol pct (GLC) | | | | |
| Aromatics . . . . . . . | 35 | 40 | 22 | 10 |
| Olefins . . . . . . . . | 9 | 7 | 11 | 9 |
| Paraffins . . . . . . . | 56 | 53 | 67 | 81 |

## Table A-5. INFLUENCE OF AMBIENT TEMPERATURE ON TOTAL HYDROCARBON EMISSION AND CONSTITUENT BENZENE IN EXHAUST FROM PROTOTYPE LOW EMISSION VEHICLES[4]

| Fuel | Ambient temperature °F | Ambient temperature °C | Total HC emissions,[a] g/mile | Benzene emissions Total HC wt. pct | Benzene emissions g/mile | Benzene emissions mg/km |
|---|---|---|---|---|---|---|
| 1972 Oldsmobile Delta 88 (Car 403) With a 455-CID Engine And Equipped With A Base-Metal Oxidation Catalyst And EGR | | | | | | |
| Typical clear I, 35 percent aromatic (7202) | 25 | -4 | 0.82 | 5.2 | 0.043 | 27 |
| | 45 | 7 | 0.45 | 7.2 | 0.032 | 12 |
| | 75 | 24 | 0.33 | 7.7 | 0.025 | 15 |
| | 95 | 35 | 0.63 | 4.7 | 0.030 | 19 |
| Indolene clear, 22 percent aromatic (7203) | 25 | -4 | 0.62 | 6.2 | 0.038 | 24 |
| | 45 | 7 | 0.44 | 6.3 | 0.028 | 17 |
| | 75 | 24 | 0.43 | 6.0 | 0.026 | 16 |
| | 95 | 35 | 0.52 | 5.2 | 0.027 | 17 |
| High alkylate, 10 percent aromatic (7212) | 25 | -4 | 0.98 | 2.0 | 0.018 | 12 |
| | 45 | 7 | 0.59 | 2.3 | 0.014 | 9 |
| | 75 | 24 | 0.50 | 2.9 | 0.015 | 9 |
| | 95 | 35 | 0.58 | 2.1 | 0.012 | 7 |
| 1972 Ford Torino (Car 724) With A 351-CID Engine and Equipped With Platinum Oxidation Catalysts And EGR | | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 24 | -4 | 4.23 | 4.3 | 0.182 | 113 |
| | 45 | 7 | 2.36 | 4.4 | 0.104 | 65 |
| | 75 | 24 | 0.72 | 4.2 | 0.030 | 19 |
| | 95 | 35 | 0.82 | 4.4 | 0.036 | 33 |
| High alkylate, 10 percent aromatic (7212) | 25 | -4 | 4.97 | 1.8 | 0.090 | 56 |
| | 45 | 7 | 3.31 | 1.7 | 0.056 | 35 |
| | 75 | 24 | 0.86 | 1.3 | 0.011 | 7 |
| | 95 | 35 | 1.06 | 1.5 | 0.016 | 1 |

(continued)

Table A-5 (continued).

| Fuel | Ambient temperature | | Total HC emissions.[a] g/mile | Benzene emissions | | |
|---|---|---|---|---|---|---|
| | °F | °C | | Total HC wt. pct | g/mile | mg/km |
| 1971 Plymouth Fury III (Car 775) With A 360-CID Engine And Equipped With The Ethyl Lean Reactors and EGR | | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 25 | -3.9 | 1.85 | 4.7 | 0.087 | 54 |
| | 45 | 7.2 | 0.74 | 5.8 | 0.043 | 27 |
| | 75 | 24 | 0.43 | 5.0 | 0.022 | 14 |
| | 95 | 35 | 0.47 | 3.7 | 0.017 | 11 |
| High alkylate, 10 percent aromatic (7212) | 25 | -3.9 | 2.15 | 1.6 | 0.034 | 21 |
| | 45 | 7.2 | 0.77 | 2.0 | 0.015 | 9 |
| | 75 | 24 | 0.36 | 1.7 | 0.006 | 4 |
| | 95 | 35 | 0.63 | 1.3 | 0.008 | 5 |

[a] Data are weighted in accordance with the 1975 Federal test procedure and each value represents the average of three replicate tests.

Table A-6. INFLUENCE OF FUEL COMPOSITION ON TOTAL HYDROCARBONS EMISSION AND CONSTITUENT BENZENE IN EXHAUST FROM 1970-1973 TEST VEHICLES[4]

| Fuel | Total[a] HC emissions |  | Benzene emission[a] |  |  |
|---|---|---|---|---|---|
|  | g/mile | g/km | Total HC wt. pct | g/mile | mg/km |
| 1972 Oldsmobile 98 (Car 151) With A 455-CID Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 1.79 | 1.11 | 4.5 | 0.081 | 50 |
| Indolene clear, 22 percent aromatic (7203) | 1.72 | 1.07 | 4.2 | 0.072 | 45 |
| 1971 Ford Galaxie (Car 707) With A 351-CID Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 4.88 | 3.03 | 4.8 | 0.234 | 145 |
| Indolene clear, 22 percent aromatic (7203) | 5.56 | 3.45 | 3.8 | 0.211 | 131 |
| 1971 Plymouth Fury III (Car 76) With A 360-CID Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 3.32 | 2.00 | 5.1 | 0.164 | 102 |
| Indolene clear, 22 percent aromatic (7203) | 3.54 | 2.20 | 4.2 | 0.149 | 93 |
| 1972 Ford Torino (Car 769) With A 351-CID Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 2.16 | 1.34 | 6.0 | 0.130 | 81 |
| Indolene clear, 22 percent aromatic (7203) | 2.29 | 1.42 | 4.5 | 0.103 | 64 |

(Continued)

Table A-6 (continued).

| Fuel | Total[a] HC emissions |  | Benzene emission[a] |  |  |
|---|---|---|---|---|---|
|  | g/mile | g/km | Total HC wt. pct | g/mile | g/km |
| 1970 Chevrolet Impala (Car 595) With A 350-CID Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 3.58 | 2.22 | 5.5 | 0.197 | 122 |
| Indolene clear, 22 percent aromatic (7203) | 3.94 | 2.45 | 4.3 | 0.169 | 105 |
| 1970 Pontiac (Car 400) With A 400-CID Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 5.86 | 3.64 | 3.9 | 0.229 | 142 |
| Indolene clear, 22 percent aromatic (7203) | 5.92 | 3.68 | 3.5 | 0.207 | 129 |
| 1970 Volkswagon (Car 365) With A 1,600-CC Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 2.44 | 1.52 | 5.2 | 0.127 | 79 |
| Indolene clear, 22 percent aromatic (7203) | 1.91 | 1.19 | 4.3 | 0.082 | 51 |
| 1971 Chevrolet Vega (Car 68) With A 2,300-CC Engine |  |  |  |  |  |
| Typical clear II, 40 percent aromatic (7221) | 4.92 | 3.06 | 3.8 | 0.187 | 116 |
| Indolene clear, 22 percent aromatic (7203) | 5.54 | 3.38 | 3.4 | 0.185 | 115 |

(Continued)

Table A-4 (continued).

| Fuel | Total[a] HC emissions g/mile | Total[a] HC emissions g/km | Benzene emission[a] Total HC wt. pct | Benzene emission[a] g/mile | Benzene emission[a] g/km |
|---|---|---|---|---|---|
| **1973 Ford Torino (Car 146) With A 351-CID Engine** | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 2.79 | 1.73 | 5.3 | 0.148 | 92 |
| Indolene clear, 22 percent aromatic (7203) | 2.68 | 1.67 | 4.2 | 0.113 | 70 |
| **1973 Chevrolet Impala (Car 110) With A 351-CID Engine** | | | | | |
| Typical clear II, 40 percent aromatic (7221) | 2.16 | 1.34 | 5.2 | 0.112 | 69 |
| Indolene clear, 22 percent aromatic (7203) | 2.12 | 1.32 | 4.3 | 0.091 | 56 |

[a] All tests were conducted at 24°C ambient temperature. Data are weighted in accordance with 1975 Federal test procedure.

Because of the minimal effect of variation in fuel aromaticity, it was concluded that HC emissions are affected mainly by changes in physical properties of the fuels (which affect carburetor metering and thus the air/fuel ratio) rather than by changes in chemical composition. Benzene in the total hydrocarbons emitted by all 10 vehicles using the higher aromatic fuel averaged 111 mg/km (0.178 g/mile). This is approximately 10 percent higher than the volume of benzene emitted from the vehicles using the lower aromatic fuel. Had the carburetor of each vehicle been adjusted for each fuel, the significant difference in the total hydrocarbon (and therefore benzene) emissions attributable to variation of fuel aromaticity might not have occurred.

# APPENDIX B

## Table B-1. U.S. REFINERIES AND THEIR PRODUCTION CAPACITIES[53]

| COMPANY | LOCATION | REFINERY[a] CAPACITY ($m^3$/day) | PRODUCTION CAPACITY | | | |
|---|---|---|---|---|---|---|
| | | | LUBES[a] ($m^3$/day) | ASPHALT[a] ($m^3$/day) | COKE[a] (metric tpd) | OPERATING[a] GASOLINE OUTPUT ($m^3$/day) |
| Adobe Refining Co. | LaBlanca, Tex. | 676 | --- | --- | --- | --- |
| Allied Materials Corp | Stroud, Okla. | 875 | 143 | 192 | --- | --- |
| Amerada-Hess | Fort Reading, N.J. | 11100 | --- | --- | --- | 5090 |
| | Purvis, Miss. | 4530 | --- | --- | 291 | 2850 |
| American Petrofina | Eldorado, Kan. | 3980 | --- | 318 | --- | 1690 |
| | Mt. Pleasant, Tex. | 4130 | --- | 1270 | --- | 1510 |
| | Port Arthur, Tex. | 13400 | --- | --- | --- | 4170 |
| Amoco Oil | Savannah, Ga. | 1910 | --- | 1270 | --- | --- |
| | Wood River, Ill. | 17000 | --- | 1720 | --- | 5470 |
| | Whiting, Ind. | 50100 | 1380 | 4930 | 663 | 20000 |
| | Baltimore, Md. | 1590 | --- | 1270 | --- | --- |
| | Sugar Creek, Mo. | 16700 | --- | 1030 | 409 | 5950 |
| | Mandan, N. Dakota | 7630 | --- | --- | --- | 3180 |
| | Texas City, Tex. | 52900 | --- | 843 | 726 | 39400 |
| | Salt Lake City, Utah | 6200 | --- | 398 | --- | 2770 |
| | Yorktown, Va. | 8430 | --- | --- | 645 | 3820 |
| | Casper, Wyoming | 6840 | 204 | 246 | --- | 1570 |
| APCO Oil Corp. | Arkansas City, Kan. | 3980 | --- | 223 | --- | 2540 |
| | Cyril, Okla. | 1910 | --- | 207 | --- | 763 |
| Arizona Fuels Corp. | Fredonia, Ariz. | 1590 | --- | --- | --- | --- |
| | Roosevelt, Utah | 1750 | --- | --- | --- | --- |
| Ashland Petroleum | Calettsburg, Ky. | 21000 | --- | 1590 | --- | 8080 |
| | Louisville, Ky. | 3980 | --- | 557 | --- | 1370 |
| | Tonawanda, N.Y. | 10300 | --- | 1590 | --- | 3500 |
| | Canton, Ohio | 9540 | --- | 1590 | --- | 4370 |
| | Findlay, Ohio (Seasonally) | 1590 | --- | 954 | --- | --- |
| Atlantic Richfield Co. | North Slope, Alaska | 763 | --- | --- | --- | --- |
| | Carson, Calif. | 26200 | --- | --- | 1630 | 13700 |
| | East Chicago, Ind. | 20000 | --- | 1650 | --- | 7600 |
| | Philadephia, Penn. | 29400 | --- | 3100 | --- | 12600 |
| | Houston, Tex. | 33900 | 1030 | --- | 1180 | 20100 |
| | Ferndale, Wash. | 15300 | --- | --- | 1360 | 9740 |
| Atlas Processing | Shreveport, La. | 4610 | --- | --- | --- | 1270 |
| Bay Refining - Dow Chem. | Bay City, Mich. | 2700 | --- | --- | --- | 525 |
| Bayou State Oil Corp. | Hosston, La. | 557 | 200 | 80 | --- | --- |
| Beacon Oil Co. | Hanford, Ca. | 1910 | --- | --- | --- | 411 |
| Berry Petroleum Co. | Stephens, Ark. | 477 | --- | 160 | --- | --- |
| Big West Oil Co. | Kevin, Mon. | 815 | --- | 52 | --- | 216 |
| B. P. Oil Corp. | Marcus Hook, Penn. | 15600 | --- | --- | --- | 7710 |
| Bradford Petroleum | Bradford, Penn. | 1110 | 493 | --- | --- | 286 |
| British Petroleum Co. | North Slope, Alaska | 200 | --- | --- | --- | --- |
| Calumet Refining Co. | Princeton, La. | 382 | 270 | 76 | --- | --- |
| Canal Refining Co. | Church Point, La. | 398 | --- | --- | --- | 200 |
| Caribon Four Corners, Inc. | Kirtland, N. Mex. | 350 | --- | --- | --- | --- |
| | Woods Cross, Utah | 668 | --- | --- | --- | 477 |

Table B-1 (continued).

| COMPANY | LOCATION | REFINERY[a] CAPACITY (m³/day) | PRODUCTION CAPACITY | | | |
|---|---|---|---|---|---|---|
| | | | LUBES[a] (m³/day) | ASPHALT[a] (m³/day) | COKE[a] (metric tpd) | OPERATING[b] GASOLINE OUTPUT (m³/day) |
| Cenex | Laurel, Mon. | 6680 | --- | --- | --- | 3070 |
| Champlin Petroleum Co. | Corpus Christi, Tex. | 9860 | --- | --- | --- | 5100 |
| | Wilmington, Calif. | 4610 | --- | --- | 522 | 398 |
| | Enid, Okla. | 7870 | 175 | 223 | 150 | 5380 |
| Charter International Oil Co. | Houston, Texas | 11100 | --- | 636 | --- | 4450 |
| Chevron Asphalt Co. | Baltimore Md. | 2150 | --- | 1750 | --- | --- |
| Chevron Oil Co. | Perth Amboy, N.J. | 14000 | --- | 3980 | --- | 3420 |
| | El Paso, Tex. | 11300 | --- | 795 | --- | 5450 |
| | Salt Lake City, Utah | 7160 | --- | --- | --- | 2850 |
| Cities Service Oil Co. | Lake Charles, La. | 42600 | 1110 | --- | 908 | 17300 |
| Clark Oil & Refining Corp. | Blue Island, Ill. | 10800 | --- | 716 | --- | 7600 |
| | Hartford, Ill. | 5720 | --- | --- | 409 | 6480 |
| Coastal States Petrochemical Co | Corpus Christi, Tex. | 21500 | --- | 80 | 454 | 7030 |
| Continental Oil Co. | Billings, Mon. | 8350 | --- | 557 | --- | 3380 |
| | Commerce C[illegible], Colo. | 4770 | --- | 525 | --- | 1700 |
| | Ponca City, Okla. | 18600 | 366 | 477 | 454 | 9410 |
| | Westlake, La. | 13200 | --- | --- | 454 | 5600 |
| | Wrenshall, Minn. | 3740 | --- | --- | --- | 1060 |
| Cosden Oil & Chemical Co. | Big Spring, Tex. | 10300 | --- | 1270 | --- | 8740 |
| Cotton Valley Solvents Co. | Cotton Valley, La. | 1230 | --- | --- | --- | --- |
| CRA Inc. | Coffeyville, Kan. | 5570 | 239 | --- | 272 | 2860 |
| | Phillipsburg, Kan. | 3180 | --- | 318 | --- | 1510 |
| | Scottsbluff, Neb. | 795 | --- | --- | --- | 350 |
| Cross Oil & Refining Co. | Smackover, Ark. | 771 | 207 | 223 | --- | --- |
| Crown Central Petroleum Corp. | Houston, Texas | 15900 | --- | --- | 272 | 8045 |
| Crystal Refining Co. | Carson City, Mich. | 986 | --- | --- | --- | --- |
| Delta Refining Co. | Memphis, Tenn. | 4610 | --- | 477 | --- | 2230 |
| Derby Refining Co. | Wichita, Kan. | 4110 | --- | --- | 145 | 2020 |
| Diamond Shamrock Oil & Gas Co. | Sunray, Texas | 7470 | --- | 398 | --- | 4130 |
| Douglas Oil Co. of Calif. | Paramount, Calif. | 5570 | --- | 2230 | --- | 986 |
| | Santa Monica, Calif. | 1300 | --- | 922 | --- | --- |
| Eddy Refining Co. | Houston, Texas | 517 | --- | --- | --- | --- |
| Edgington Oil Co. | Long Beach, Calif. | 4610 | --- | 1190 | --- | --- |
| Edgington Oxnard Refinery | Oxnard, Calif. | 398 | --- | --- | --- | --- |
| Evangeline Refining Co., Inc. | Jenings, La. | 684 | --- | --- | --- | 95 |
| Exxon Oil Co. | Benica, Calif. | 13800 | --- | --- | 817 | 12000 |
| | Baytown, Tex. | 63600 | 3980 | 1910 | --- | 26500 |
| | Baton Rouge, La. | 70800 | 2390 | 4600 | 1960 | 33000 |
| | Billings, Mon. | 7160 | --- | 2070 | 227 | 3700 |
| | Lindon, N.J. | 43700 | --- | 7310 | --- | 18400 |
| Famariss Oil Corp. | Monument, N. Mex. | 795 | --- | --- | --- | 95 |
| Fletcher Oil & Refining Co. | Carson, Calif. | 2510 | --- | --- | --- | 557 |
| Flint Chem. Co. | San Antonio, Tex. | 191 | --- | --- | --- | --- |
| Gary Western Co. | Grand Junction, Colo. | 1320 | --- | --- | 363 | --- |
| Getty Oil Co., Inc. | Delaware City, Del. | 22300 | --- | --- | 1630 | 11700 |

Table B-1 (continued).

| COMPANY | LOCATION | REFINERY[a] CAPACITY ($m^3$/day) | PRODUCTION CAPACITY LUBES[a] ($m^3$/day) | PRODUCTION CAPACITY ASPHALT[a] ($m^3$/day) | PRODUCTION CAPACITY COKE[a] (metric tpd) | OPERATING[b] GASOLINE OUTPUT ($m^3$/day) |
|---|---|---|---|---|---|---|
| Gladieux Refinery | Fort Wayne, Inc. | 1590 | --- | --- | --- | 40 |
| Golden Bear, Div. | Oildale, Calif. | 1670 | 636 | 509 | --- | --- |
| Golden Eagle Refining | Carson, Calif. | 2070 | --- | --- | --- | --- |
| Good Hope Refineries | Good Hope, La. | 4680 | --- | --- | --- | 557 |
| Gulf Oil Co. | Sante Fe Springs, Calif. | 8190 | --- | 636 | --- | 4530 |
|  | Belle Chasse, La. | 28700 | --- | --- | 763 | 16900 |
|  | Venice, La. | 4560 | --- | --- | --- | 3550 |
|  | Cleves, Ohio | 6590 | --- | 461 | --- | 3620 |
|  | Toledo, Ohio | 8000 | --- | 318 | --- | 3790 |
|  | Philadelphia, Penn. | 26800 | --- | --- | --- | 15300 |
|  | Port Arthur, Tex. | 49600 | 2010 | --- | 1260 | 26500 |
| Hawaiian Indep. Ref. | Barber's Point, Hawaii | 4770 | --- | --- | --- | --- |
| Howell Hydrocarbons | San Antonio, Texas | 493 | --- | --- | --- | 159 |
| Hunt Oil | Tuscaloosa, Ala. | 2390 | --- | 827 | --- | 191 |
| Husky Oil | North Salt Lake, Utah | 1830 | --- | --- | --- | 652 |
|  | Cheyenne, Wy. | 3750 | --- | 477 | --- | 2040 |
|  | Cody, Wy. | 1700 | --- | 636 | --- | 763 |
| Ind. Farm Bur. Coop. | Mt. Vernon, Ind. | 2390 | --- | --- | --- | 986 |
| Jet Fuel Refinery | Mosby, Mon. | 159 | --- | --- | --- | --- |
| Kern County Refining Co. | Bakersfield, Calif. | 2050 | --- | --- | --- | 509 |
| Kerr McGee Corp. | Cotton Valley, La. | 1190 | --- | --- | --- | 553 |
|  | Wynnewood, Okla. | 5090 | --- | 557 | --- | 3930 |
| Koch Refining Co. | Pine Bend, Minn. | 17000 | --- | 3180 | 1180 | 6730 |
| LaGloria Oil & Gas Co. | Tyler, Texas | 4450 | --- | --- | 73 | 2730 |
| LaJet Inc. | St. James, La. | 1750 | --- | --- | --- | --- |
| Lakeside Refining Co. | Kalamazoo, Mich. | 954 | --- | --- | --- | 191 |
| Laketon Asphalt Refining, Inc. | Laketon, Ind. | 1350 | --- | 413 | --- | --- |
| Lion Oil Co. | El Dorado, Ark. | 7000 | 127 | 954 | --- | 2660 |
| Little America Refining Co. | Casper, Wy. | 3500 | --- | 318 | --- | 1700 |
| Longview Refining Co. | Longview, Tex. | 1050 | --- | --- | --- | 239 |
| Lunday-Thagard Oil Co. | South Gate, Calif. | 795 | --- | 254 | --- | --- |
| MacMillan Ring - Free Oil Co., Inc. | Norphlet, Ark. | 716 | --- | 199 | --- | --- |
|  | Signal Hill, Calif. | 1510 | --- | --- | --- | --- |
| Marathon Oil Co. | Robinson, Ill. | 31000 | --- | --- | 817 | 11100 |
|  | Detroit, Mich. | 9220 | --- | 1380 | --- | 4640 |
|  | Texas City, Texas | 9700 | --- | --- | --- | 3130 |
| Marion Corp. | Mobile, Ala. | 2390 | --- | --- | --- | --- |
| Mid America Refinery Co., Inc. | Chanote, Kan. | 493 | --- | --- | --- | --- |
| Midland Cooperatives, Inc. | Cushing, Okla. | 3020 | --- | --- | 73 | 1540 |
| Mobil Oil Corp. | Ferndale, Wash. | 11400 | --- | --- | --- | 4320 |
|  | Beaumont, Texas | 51700 | 1400 | 16 | 1090 | 25600 |
|  | Buffalo, N.Y. | 6770 | --- | 1190 | --- | 3200 |
|  | Paulsboro, N.J. | 15600 | 1020 | --- | 885 | 5660 |
|  | Augusta, Kan. | 7950 | --- | 1270 | --- | 3650 |
|  | Torrance, Calif. | 19600 | --- | --- | 2540 | 14100 |

Table B-1 (continued).

| COMPANY | LOCATION | REFINERY[a] CAPACITY ($m^3$/day) | PRODUCTION CAPACITY | | | |
|---|---|---|---|---|---|---|
| | | | LUBES[a] ($m^3$/day) | ASPHALT[a] ($m^3$/day) | COKE[a] (metric tpd) | OPERATING[b] GASOLINE OUTPUT ($m^3$/day) |
| Mobile Oil Corp., Inc. | Joliet, Ill. | 27800 | --- | --- | 1540 | 14500 |
| | East Chicago, Ind. | 7470 | --- | --- | --- | 3670 |
| Mohawk Petroleum Corp., Inc. | Bakersfield, Calif. | 3510 | --- | --- | --- | 350 |
| Mountaineer Refining Co., Inc. | LaBarge, Wy. | 80 | --- | --- | --- | --- |
| Murphy Oil Corp. | Meraux, La. | 14700 | --- | --- | --- | 3690 |
| | Superior, Wisc. | 5880 | --- | 1910 | --- | 2240 |
| National Cooperative Ref. Assoc | McPherson, Kan. | 8610 | --- | --- | 318 | 3350 |
| Navajo Refining Co. | Artesia, N. Mex. | 3330 | --- | 223 | --- | 914 |
| Newhall Refining Co., Inc.* | Newhall, Calif. | 1150 | --- | 477 | --- | --- |
| North American Petroleum Corp | Shallow Water, Kan. | 795 | --- | --- | --- | --- |
| Northwestern Refining Co. | St. Paul Park, Minn. | 9540 | --- | 3500 | --- | 3330 |
| OKC Refining Inc. | Okmulgee, Okla. | 3420 | --- | 223 | --- | 1990 |
| Osceola Refining Co. | West Branch, Mich. | 1510 | --- | --- | ---- | --- |
| Pasco, Inc. | Sinclair, Wy. | 6360 | --- | 366 | --- | 2630 |
| Pennzoil Co. | Rouseville, Penn. | 1590 | 561 | --- | --- | 448 |
| | Falling Rock, W. Va. | 795 | 207 | --- | --- | 318 |
| Phillips Petroleum Co. | Borger, Tex. | 15100 | --- | --- | --- | 10600 |
| | Kansas City, Kan. | 13500 | 398 | 477 | --- | 6121 |
| | Great Falls, Mon. | 906 | --- | 127 | --- | 262 |
| | Woods Cross, Utah | 3660 | --- | 350 | --- | 1750 |
| | Sweeney, Texas | 13500 | --- | --- | --- | 9060 |
| | Avon, Calif. | 17500 | 266 | --- | 1090 | 13600 |
| Plateau, Inc. | Bloomfield, N.Mex. | 811 | --- | --- | --- | 350 |
| Powerline Oil Co. | Santa Fe Springs, Calif. | 4530 | --- | 795 | --- | 2130 |
| Pride Refining Inc. | Abilene, Tex. | 2240 | --- | --- | --- | --- |
| Quaker State Oil Ref. Corp. | Emlenton, Penn. | 528 | 270 | --- | --- | 169 |
| | Farmers Valley, Penn. | 1030 | 398 | --- | --- | 366 |
| | Newell, W. Va. | 1540 | 572 | --- | --- | 398 |
| | St. Mary's, W. Va. | 771 | 270 | --- | --- | 183 |
| Quintana-Howell | Corpus Christi, Tex. | 1590 | --- | --- | --- | --- |
| Rock Island Refining Corp. | Indianapolis, Ind. | 4690 | --- | 477 | --- | 2500 |
| Sage Creek Refining | Cowley, Wy. | 159 | --- | --- | --- | --- |
| San Joaquin Refining | Oildale, Calif. | 2700 | --- | 534 | --- | --- |
| Sequoia Refining Corp. | Hercules, Calif. | 4290 | --- | --- | --- | 2660 |
| Seminole Asphalt Ref. | St. Marks, Fla. | 795 | --- | 393 | --- | --- |
| Shell Oil Co. | Martinez, Calif. | 15900 | 716 | 1650 | --- | 7880 |
| | Wilmington, Calif. | 15300 | --- | --- | 1630 | 7360 |
| | Wood River, Ill. | 41300 | 890 | 3580 | --- | 24800 |
| | Norco, La. | 38200 | --- | 954 | 817 | 20200 |
| | Ciniza, N.Mex. | 3180 | --- | 134 | --- | 1830 |
| | Deer Park, Tex. | 45800 | 954 | 604 | --- | 19100 |
| | Odessa, Tex. | 5090 | --- | --- | --- | 2420 |
| | Anacortes, Wash. | 14500 | --- | --- | --- | 7710 |
| Shelly Oil Co. | El Dorado, Kan. | 11700 | --- | --- | 454 | 6150 |
| Somerset Refinery | Somerset, Ky. | 445 | --- | --- | --- | --- |
| Sound Refining Inc. | Tacoma, Wash. | 716 | 302 | 413 | --- | --- |
| Southland Oil Co. | Crupp, Miss. | 668 | --- | 229 | --- | --- |

Table B-1 (continued).

| COMPANY | LOCATION | REFINERY$^a$ CAPACITY ($m^3$/day) | PRODUCTION CAPACITY |  |  | OPERATING$^b$ GASOLINE OUTPUT ($m^3$/day) |
|---|---|---|---|---|---|---|
|  |  |  | LUBES$^a$ ($m^3$/day) | ASPHALT$^a$ ($m^3$/day) | COKE$^a$ (metric tpd) |  |
| **Southland Oil Co.** | Lumberton, Miss. | 954 | --- | 372 | --- | --- |
|  | Sandersville, Miss. | 1750 | --- | 554 | --- | --- |
| **Southwestern Oil & Ref. Co.** | Corpus Christi, Tex. | 15900 | --- | --- | --- | 3720 |
| **Southwestern Ref. Co.** | LaBarge, Wy. | 52 | --- | --- | --- | --- |
| **Standard Oil of Calif.** | Kenai, Alaska | 3500 | --- | 48 | --- | --- |
|  | Bakersfield, Calif. | 4130 | --- | 175 | --- | 1160 |
|  | El Segundo, Calif. | 36600 | --- | 1320 | 2000 | 21400 |
|  | Richmond, Calif. | 30200 | 1590 | 1750 | --- | 20300 |
|  | Barber's Point, Hawaii | 6360 | --- | 207 | --- | 1860 |
|  | Portland, Oregon | 2230 | --- | 1370 | --- | --- |
|  | Richmond Beach, Wash. | 716 | --- | 636 | --- | --- |
| **Standard Oil of Ky.** | Pascagoula, Miss. | 38200 | --- | --- | --- | 22800 |
| **Standard Oil of Ohio** | Lima, Ohio | 26200 | 334 | --- | 554 | 8700 |
|  | Toledo, Ohio | 19100 | --- | 1110 | 590 | 8700 |
| **Sun Oil Co.** | Toledo, Ohio | 19900 | --- | --- | --- | 13800 |
|  | Duncan, Okla | 7710 | --- | --- | 363 | 4390 |
|  | Tulsa, Okla. | 14100 | --- | 668 | 272 | 6420 |
|  | Marcus Hook, Penn. | 26200 | 2700 | 1910 | --- | 13500 |
| **Sunland Ref. Co.** | Bakersfield, Calif. | 1400 | --- | --- | --- | 151 |
| **Suntide Refining** | Corpus Christi, Tex. | 9060 | --- | --- | 213 | 4710 |
| **Tenneco Oil Co.** | Bakersfield, Calif. | 191 | --- | --- | --- | --- |
|  | Chalmette, La. | 15400 | --- | --- | 318 | 9810 |
| **Tesoro-Alaskan Petr.** | Kenai, Alaska | 6040 | --- | --- | --- | --- |
| **Tesoro Petroleum** | Wolf Point, Mon. | 398 | --- | --- | --- | --- |
|  | Carrizo Springs, Tex. | 2070 | --- | --- | --- | --- |
|  | Newcastle, Wy. | 1670 | --- | --- | --- | 477 |
| **Texaco, Inc.** | Wilmington, Calif. | 11900 | --- | --- | 1500 | 11800 |
|  | Lawrenceville, Ill. | 13400 | --- | 429 | --- | 7080 |
|  | Lockport, Ill. | 11400 | --- | --- | 272 | 5990 |
|  | Convent, La. | 22300 | --- | --- | --- | 1230 |
|  | Westville, N.J. | 14000 | --- | --- | --- | 5250 |
|  | Anacortes, Wash. | 10000 | --- | --- | --- | 3550 |
|  | Casper, Wy. | 3340 | --- | 239 | 114 | 1500 |
|  | Port Arthur, Tex. | 64600 | 3180 | --- | --- | 26200 |
|  | Amarillo, Tex. | 3180 | --- | --- | 91 | 1620 |
|  | El Paso, Tex. | 2700 | --- | --- | 91 | 1510 |
|  | West Tulsa, Okla. | 7950 | --- | --- | --- | 3580 |
|  | Port Neches, Tex. | 7470 | --- | 1430 | --- | --- |
| **Texas Asphalt & Ref. Co.** | Fort Worth, Tex. | 477 | --- | --- | --- | --- |
| **Texas City Refining** | Texas City, Tex. | 9540 | --- | --- | --- | 3550 |
| **The Refinery Corp.** | Commerce City, Colo. | 2780 | --- | --- | --- | 2590 |
| **Three Rivers Refinery** | Three Rivers, Tex. | 238 | 127 | 19 | --- | --- |
| **Thriftway Co.** | Bloomfield, N. Mex. | 338 | --- | --- | --- | --- |
| **Tonkawa Refining** | Tonkawa, Okla. | 954 | --- | --- | --- | --- |
| **Toscopetro Corp.** | Bakersfield, Calif. | 4220 | --- | --- | 191 | 4300 |
| **Total Leonard, Inc.** | Alma, Mich. | 6500 | --- | 477 | --- | 3530 |
| **U.S. Oil & Refining** | Tacoma, Wash. | 2540 | --- | 477 | --- | 398 |

## Table B-1 (continued).

| COMPANY | LOCATION | REFINERY[a] CAPACITY ($m^3$/day) | PRODUCTION CAPACITY | | | |
|---|---|---|---|---|---|---|
| | | | LUBES[a] ($m^3$/day) | ASPHALT[a] ($m^3$/day) | COKE[a] (metric tpd) | OPERATING[b] GASOLINE OUTPUT ($m^3$/day) |
| Union Oil Co. of Calif. | Los Angeles, Calif. | 17200 | --- | 1590 | --- | 8780 |
| | San Francisco, Calif. | 17600 | 572 | 978 | 1680 | 11100 |
| | Lemont, Ill. | 24200 | --- | 318 | 908 | 11300 |
| | Nederland, Tex. | 18400 | 557 | 859 | --- | 8060 |
| Union Texas Petroleum | Winnie, Tex. | 1510 | --- | --- | --- | 1256 |
| United Refining Co. | Warren, Penn. | 6040 | --- | 636 | --- | 2290 |
| Valvoline Oil Co. | Freedom, Penn. | 986 | 207 | --- | --- | --- |
| Vickers Petroleum | Ardmore, Okla. | 5000 | --- | 795 | --- | 2610 |
| Vulcan Asphalt Ref. | Cordova, Ala. | 477 | --- | --- | --- | --- |
| Warrior Asphalt Co. | Holt, Ala. | 385 | --- | 274 | --- | --- |
| West Coast Oil Co. | Bakersfield, Calif. | 2540 | --- | 636 | --- | 318 |
| Westco Refining Co. | Cut Bank, Mon. | 741 | --- | --- | --- | 242 |
| Westland Oil Co. | Williston, N.D. | 741 | --- | --- | --- | 318 |
| Winston Refining | Fort Worth, Tex. | 2390 | --- | --- | --- | 405 |
| Wireback Oil Co. | Plymouth, Ill. | 238 | --- | --- | --- | --- |
| Wolf's Head Oil Ref. | Reno, Penn. | 334 | 80 | --- | --- | --- |
| Yetter Oil Co. | Colmar, Ill. | 159 | --- | --- | --- | --- |
| Young Refining Corp. | Douglasville, Ga. | 398 | --- | 207 | --- | --- |
| **TOTAL** | | **2262864** | **32531** | **107073** | **30628** | **1062858** |

Source: (a) "Annual Refining Survey," Oil & Gas J. 1 April 1974.

(b) National Petroleum News, Fact Book, Mid-May 1974, N.Y., McGraw-Hill, 1974.

Table B-2. PETROLEUM-BASED BENZENE PRODUCERS (1976)[28]

| Company | Location | Benzene Capacity,[a] $10^6$ gal |
|---|---|---|
| Allied Chemical | Winnie, Texas | 3 |
| Amerada Hess Corp. | St. Croix, Virgin Islands | 25 |
| American Petrofina, Inc. | Big Spring, Texas | 45 |
|  | Port Arthur, Texas | 15 |
| Ashland Oil, Inc. | Ashland, Kentucky | 50 |
|  | North Tonawanda, New York | 15 |
| Atlantic Richfield Co. | Houston, Texas | 44 |
|  | Wilmington, California | 12 |
| Charter International Oil Co. | Houston, Texas | 5 |
| Cities Service Co., Inc. | Lake Charles, Louisiana | 25 |
| Coastal States Gas Prod. Co. | Corpus Christi, Texas | 70 |
| Commonwealth Oil Refining Co. | Penuelas, Puerto Rico | 185 |
| Crown Central Petroleum Corp. | Pasadena, Texas | 23 |
| Dow Chemical Co. | Bay City, Michigan | 30 |
|  | Freeport, Texas | 50 |
| Exxon Corp. | Baton Rouge, Louisiana | 65 |
|  | Baytown, Texas | 62 |
| Gulf Oil Corporation | Alliance, Louisiana | 70 |
|  | Philadelphia, Pa. | 33 |
|  | Port Arthur, Texas | 38 |
| Kerr-McGee Corp. | Corpus Christi, Texas | 16 |
| Marathon Oil Co. | Texas City, Texas | 6 |
| Mobil Oil Corp. | Beaumont, Texas | 60 |
| Monsanto Co. | Chocolate Bayou, Texas | 75 |
| Pennzoil United, Inc. | Shreveport, Louisiana | 15 |
| Phillips Petrol. Co. | Sweeny, Texas | 22 |
|  | Guayama, Puerto Rico | 110 |
| Shell Oil Co. | Deer Park, Texas | 75 |
|  | Odessa, Texas | 6 |
|  | Wood River, Illinois | 40 |
| Skelly Oil Company | El Dorado, Kansas | 13 |
| Southwestern Oil & Ref. Co. |  |  |
| Standard Oil Co. of California | El Segundo, California | 23 |
| Standard Oil Co. (Ind.) | Texas City, Texas | 85 |
| Standard Oil Co. (Ohio) | Marcus Hook, Pa. | 8 |
| Sun Oil Co. | Marcus Hook, Pa. | 15 |
|  | Corpus Christi, Texas | 35 |
|  | Tulsa, Oklahoma | 24 |
| Tenneco, Inc. | Chalmette, Louisiana | 10 |
| Texaco, Inc. | Port Arthur, Texas | 45 |
|  | Westville, N.J. | 35 |
| Union Carbide Corp. | Taft, Louisiana | 70 |
| Union Oil Co. of California | Lemont, Illinois | 19 |
| Union Oil-American Petrofina | Beaumont, Texas | 19 |
| Union Pacific Corp. | Corpus Christi, Texas | 10 |
|  | **Total** | **1,701** |

[a] To convert to cubic meters multiply by $3.785 \times 10^{-3}$.

# APPENDIX C

## Table C-1. COAL-DERIVED BENZENE PRODUCTION FACILITIES (1976)[26]

| Company | Location | Benzene capacity January 1, 1976 | |
|---|---|---|---|
| | | $10^6$ gal | $km^3$ |
| Armco Steel Corp. | Middletown, Ohio | 3 | 11 |
| Bethlehem Steel Corp. | Bethlehem, Pa. | 4 | 15 |
| | Lackawanna, N.Y. | 8 | 30 |
| | Sparrows Point, Maryland | 15 | 57 |
| C.F. & I. Steel Corp. | Pueblo, Colorado | 3 | 11 |
| Interlake, Inc. | Toledo, Ohio | 1 | 4 |
| Jones & Laughlin Steel Corp. | Aliquippa, Pa. | 10 | 38 |
| Northwest Industries, Inc. | Lone Star, Texas | 1 | 4 |
| U.S. Steel Corp. | Clairton, Pa. | 45 | 170 |
| | Geneva, Utah | 4 | 15 |
| | Total | 94 | 355 |

# APPENDIX D

# Table D-1. LOCATIONS AND CAPACITIES OF ORGANIC CHEMICAL PLANTS UTILIZING BENZENE FEEDSTOCKS[28]

| Company | Location | Capacity Production[a] January 1, 1976, millions of lb | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Nitrobenzene | Aniline | Ethylbenzene | Styrene | Maleic anhydride | Cumene | Phenol | Monochlorobenzene | Dichlorobenzene (O- and P-) | Cyclohexane[b] | Detergent alkylate (Linear and Branched) |
| Allied Chemical Corp. | Syracuse, N.Y.<br>Moundsville, W. Va.<br>Frankford, Pa. | 55 | | | | 60 | | 550 | 25 | 20 | | |
| American Cyanamid Co. | Bound Brook, N.J.<br>Willow Island, W. Va. | 85<br>60 | 60<br>50 | | | | | | | | | |
| American Petrofina, Inc. | Big Spring, Tex. | | | 45 | 90 | | | | | | 12 | |
| Arco/Polymers, Inc. | Houston, Tex.<br>Port Arthur, Tex.<br>Beaver Valley, Pa. | | | 100<br>440 | 100<br>440 | | | | | | | |
| Ashland Oil, Inc. | Ashland, Ky. | | | | | | 350 | | | | | |
| The Charter Co. | Houston, Tex. | | | 35 | | | | | | | | |
| Chemical Products, Corp. | Cartersville, Ga. | | | | | | | | | 24 | | |
| Clark Oil and Refining, Inc. | Blue Island, Ill. | | | | | | 110 | 88 | | | | |
| Coastal States Gas, Corp. | Corpus Christi, Tex. | | | | | | 140 | | | | | |
| Commonwealth Oil Refining Co. | Penuelas, P.R. | | | 160 | | | | | | | 40 | |
| Continental Oil Co. | Baltimore, M.D. | | | | | | | | | | | |
| Cos-Mar, Inc. | Carville, La. | | | 720 | 600 | | | | | | | 215 |
| Dow Chem., U.S.A. | Freeport, Tex.<br>Midland, Mich.<br>Oyster Creek, Tex. | | | 1065<br>550 | 1430<br>600 | | 10 | 48<br>400 | 300 | 63 | | |
| E.I. du Pont de Nemoirs and Co. | Beaumont, Tex.<br>Gibbstown, N.J. | 310<br>200 | 200<br>130 | | | | | | | | | |
| El Paso Natural Gas Co. | Odessa, Tex. | | | 275 | 150 | | | | | | | |
| Exxon Corp. | Baytown, Tex. | | | | | | | | | | | |
| Ferro Corp. | Santa Fe Springs, Cal. | | | | | | | N.A. | | | 40 | |
| First Mississippi Corp. | Pascagoula, Miss. | 135 | 100 | | | | | | | | | |
| Foster Grant Co., Inc. | Baton Rouge, La. | | | 970 | 820 | | | | | | | |
| Georgia Pacific Corp. | Plaquemine, La. | | | | | | | 265 | | | | |
| Gulf Oil Corp. | Welcome, La<br>Philadelphia, PA<br>Port Arthur, Tex. | | | 550 | 525 | | 450<br>450 | | | | | |
| ICC Industries, Inc. | Niagara Falls, N.Y. | | | | | | | | | | 33 | |
| Joe Oil, Inc. | Houston, Tex. | | | N.A. | | | | | N.A. | N.A. | | |
| Kalama Chemical, Inc. | Kalama, Wash. | | | | | | | 55 | | | | |
| Koppers Co., Inc. | Bridgeville, Pa.<br>Cicero, Ill.<br>Follansbee, W. Va. | | | | | 34<br>10 | | N.A. | | | | |

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TABLE D-1 (continued).

| Company | Location | Capacity Production[a] January 1, 1976 (millions of lbs.) Nitro-benzene | Aniline | Ethyl-benzene | Styrene | Maleic anhydride | Cumene | Phenol | Mono-Chloro-benzene | Dichloro-benzene (O- and P-) | Cyclohexane[b] | Detergent alkylate (Linear and Branched) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Marathon Oil Co. | Texas City, Tex. | | | | | | 190 | | | | | |
| The Merichem Co. | Houston, Tex. | | | | | | | N.A. | | | | |
| Mobay Chemical Corp. | New Martinsville, W. Va | 135 | 100 | | | | | | | | | |
| Monsanto Co. | Chocolate Bayou, Tex. | | | [c] | | | 650 | 500 | | | | 225 |
| | Sauget, Ill. | 10 | | | | | | | 115 | 28 | | |
| | Texas City, Tex. | | | [c] | 1300 | | | | | | | |
| | St. Louis, Mo. | | | | | 105 | | | | | | |
| Montrose Chemical, Corp. of California | Henderson, Nev. | | | | | | | | 70 | | | |
| Occidental Petroleum, Corp. | Niagara Falls, N.Y. | | | | | | | | 15 | | | |
| PPG Industries, Inc. | Natrium, W. Va | | | | | | | | 90 | 50 | | |
| Petro-Tex Chemical, Corp. | Houston, Texas | | | | | 50 | | | | | | |
| Phillips Petroleum Co. | Borger, Texas | | | | | | | | | | | |
| | Sweeney, Tex. | | | | | | | | | | 40 | |
| | Guayama, P.R. | | | | | | | | | | 65 | |
| | Phillips, Tex. | | | N.A. | | | | | | | 70 | |
| Reichhold Chemicals, Inc. | Tuscaloosa, Ala. | | | | | | | 150 | | | | |
| | Elizabeth, N.J. | | | | | 30 | | | | | | |
| | Morris, Ill. | | | | | 60 | | | | | | |
| Rubicon Chemicals, Inc. | Geismar, La. | 75 | 55 | | | | | | | | | |
| Skelly Oil Co. | El Dorado, Kans. | | | | | | 135 | 95 | | | | |
| Solvent Chemical Co., Inc. | Malden, Mass. | | | | | | | | N.A. | 3[d] | | |
| | Niagara Falls, N.Y. | | | | | | | | N.A. | 20 | | |
| Specialty Organics, Inc. | Irwindale, Cal. | | | | | | | | | 3 | | |
| Standard Chlorine Chemical Co., Inc. | Delaware City, Del. | | | | | | | | 75 | 60[e] | | |
| | Kearny, N.J. | | | | | | | | | 16[d] | | |
| Standard Oil Co. of California | El Segundo, Cal. | | | | | | 100 | | | | | |
| | Richmond, Cal. | | | | | | | 55 | | | | 220 |
| Standard Oil (Ind.) | Texas City, Tex. | | | 945 | 840 | | 50 | | | | | |
| Stimson Lumber Co. | [illegible], Wash. | | | | | | | N.A. | | | | |
| Sun Oil Co. | Corpus Christi, Tex. | | | 95 | 80 | | 250 | | | | | |
| Tenneco, Inc. | Chalmette, La | | | 26 | | | | | | | | |
| | Fords, N.J. | | | | | 46 | | | | | | |
| Texaco, Inc. | Westville, N.J. | | | | | | 260 | | | | | |
| | Port Arthur, Tex. | | | | | | | | | | 40 | |
| Union Carbide, Corp. | Penuelas, P.R. | | | | | | 640 | 200 | | | | |
| | Seadrift, Tex. | | | 340 | 300 | | | | | | | |
| | Bound Brook, N.J. | | | | | | | 150 | | | | |
| | Charleston, W. Va. | | | | | | | | | | | |
| Union Oil Co. of California | Beaumont, Tex | | | | | | | | | | 34 | 150 |
| Union Pacific Corp. | Corpus Christi, Tex. | | | | | | | | | | 22 | |
| United States Steel | Neville Island, Pa. | | | | | 40 | | | | | | |
| | Clairton, Pa. | | | | | | | N.A. | | | | |
| | Haverhill, Ohio | | | | | | | 200 | | | | |
| Witco Chemical Corp. | Carson, Cal. | | | | | | | | | | | 55 |
| TOTALS | | 1065 | 693 | 8566 | 7075 | 415 | 3785 | 2756 | 690 | 265 | 416 | 865 |

[a] To convert to kilograms multiply by 0.454.

[b] Production capacity in millions of gallons.

[c] Combined ethylbenzene production at Chocolate Bayou, Texas and at Texas City, Texas equals 1450. Separate values not available.

[d] Production capacity for o-dichlorobenzene only.

[e] Production capacity for p-dichlorobenzene only.

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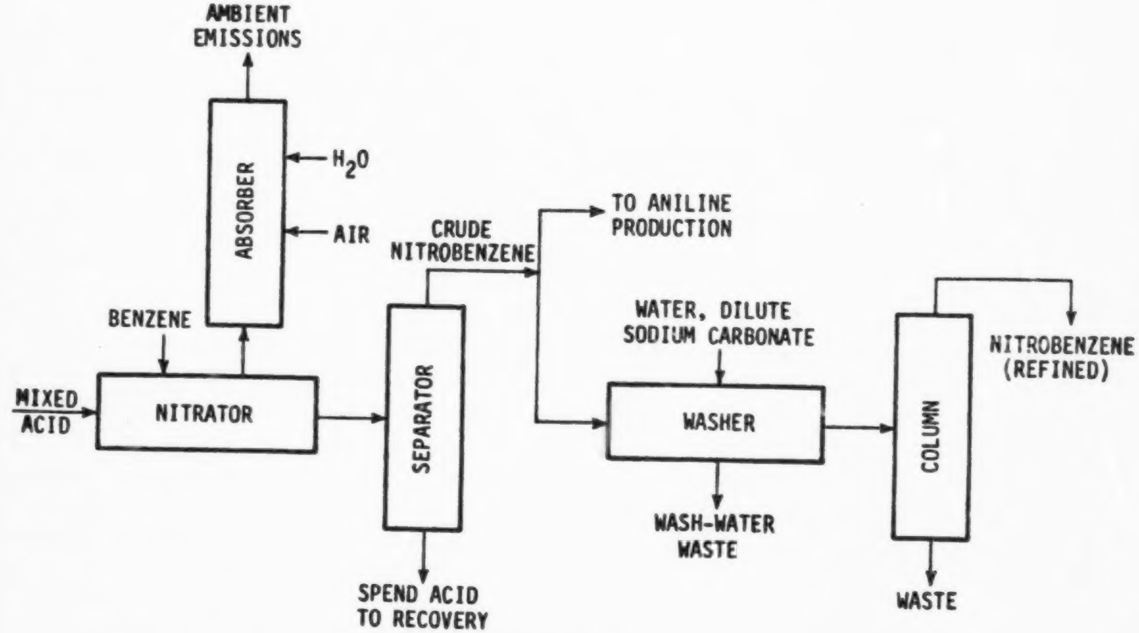
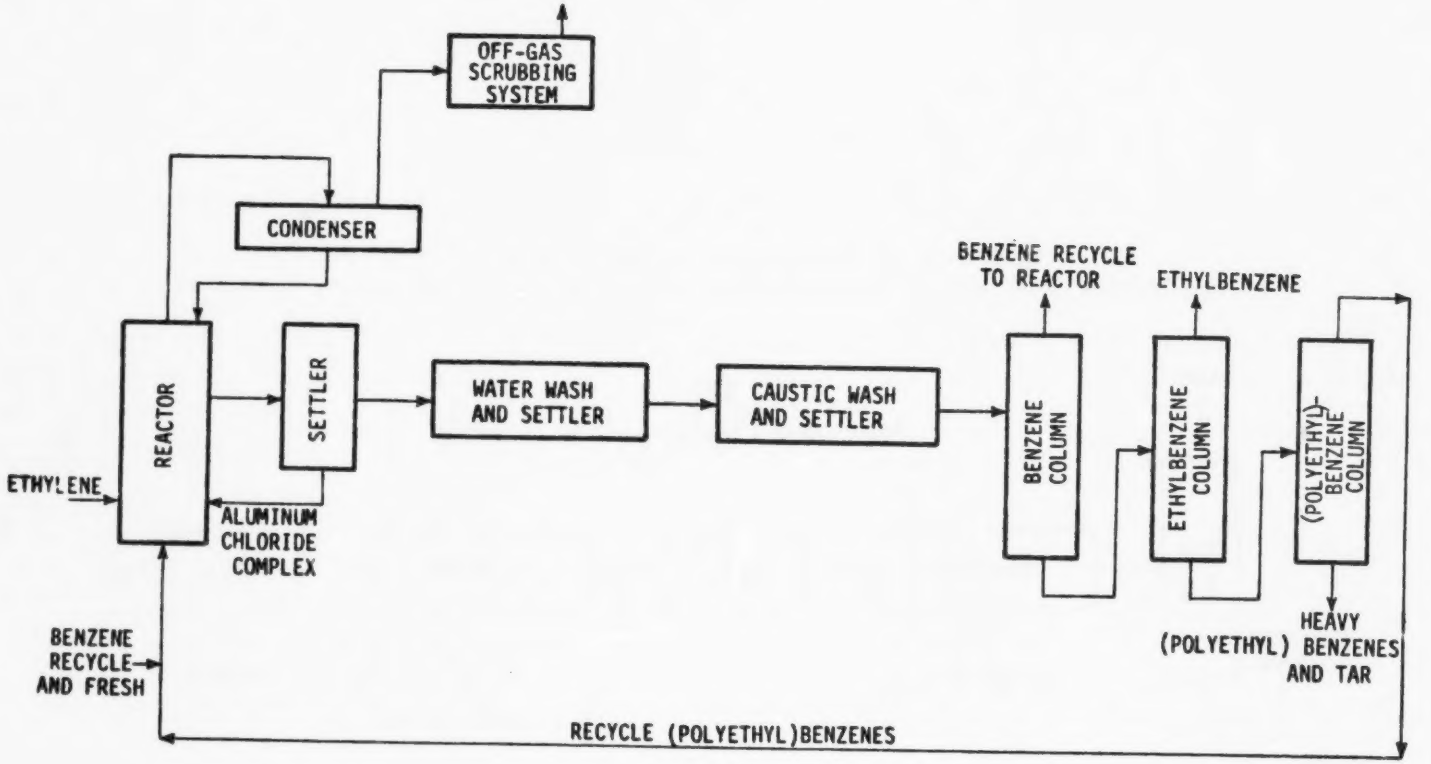

AMBIENT EMISSIONS
ABSORBER
H2O
AIR
BENZENE
MIXED ACID
NITRATOR
SEPARATOR
SPEND ACID TO RECOVERY
CRUDE NITROBENZENE
TO ANILINE PRODUCTION
WATER, DILUTE SODIUM CARBONATE
WASHER
WASH-WATER WASTE
COLUMN
NITROBENZENE (REFINED)
WASTE

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Figure D-1. Flow chart for nitrobenzene manufacture from benzene and nitric acid.

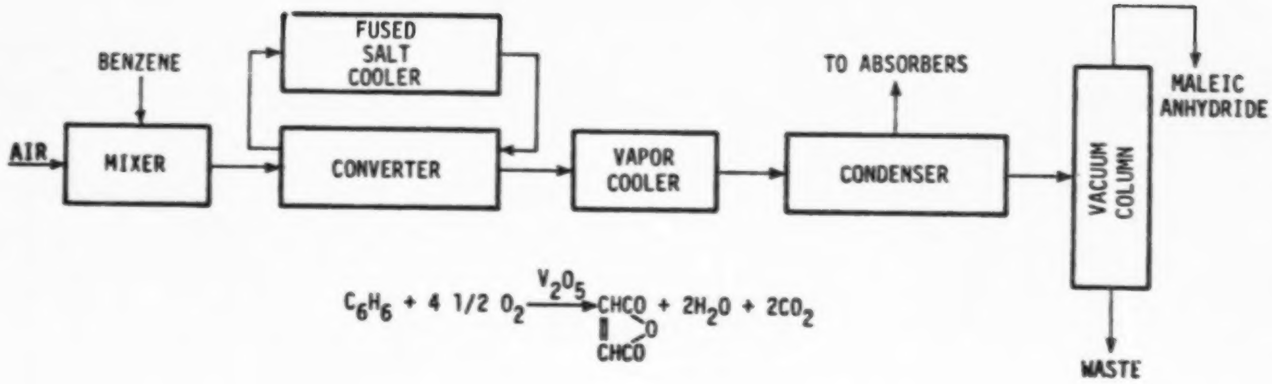
Source: Ref. 59.


OFF-GAS SCRUBBING SYSTEM
CONDENSER
REACTOR
SETTLER
WATER WASH AND SETTLER
CAUSTIC WASH AND SETTLER
BENZENE RECYCLE TO REACTOR
BENZENE COLUMN
ETHYLBENZENE
ETHYLBENZENE COLUMN
(POLYETHYL)-BENZENE COLUMN
ETHYLENE
ALUMINUM CHLORIDE COMPLEX
BENZENE RECYCLE AND FRESH
HEAVY (POLYETHYL) BENZENES AND TAR
RECYCLE (POLYETHYL)BENZENES

$$C_6H_6 + C_2H_4 \xrightarrow{AlCl_3} C_6H_5C_2H_5$$

Figure D-2. Flow chart for ethylbenzene manufacture from benzene and ethylene.

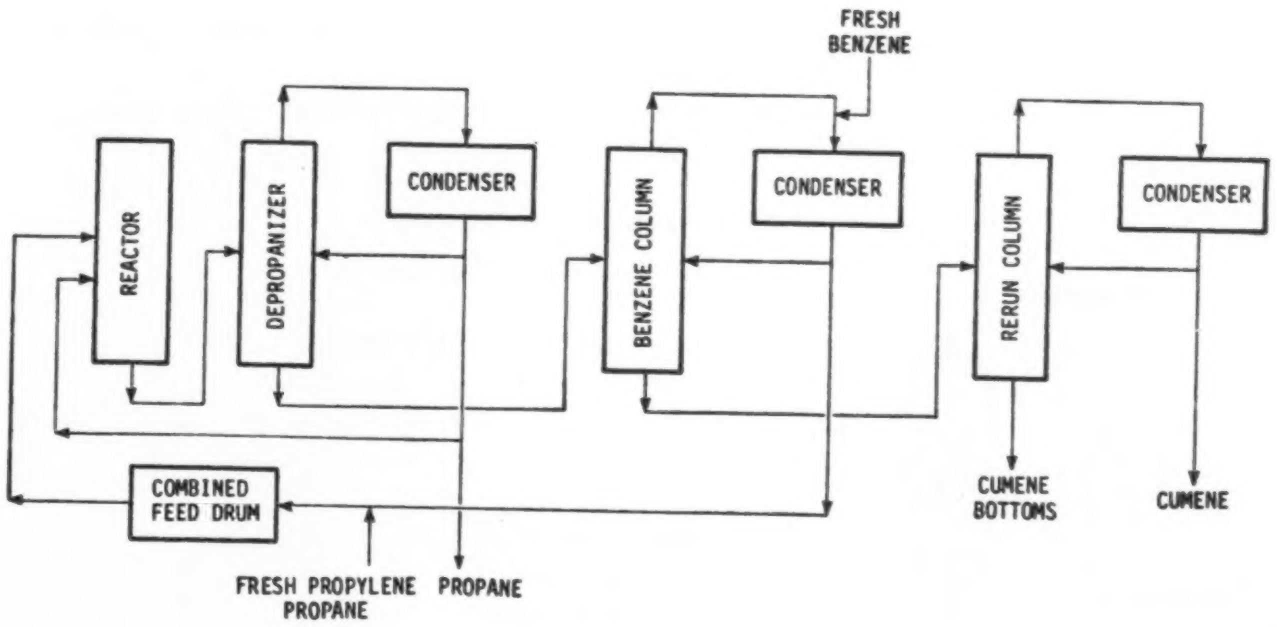
Source: Ref. 81


AIR
BENZENE
MIXER
FUSED SALT COOLER
CONVERTER
VAPOR COOLER
TO ABSORBERS
CONDENSER
VACUUM COLUMN
MALEIC ANHYDRIDE
WASTE

$$C_6H_6 + 4\ 1/2\ O_2 \xrightarrow{V_2O_5} \begin{matrix}CHCO\\ \| \quad \rangle O\\ CHCO\end{matrix} + 2H_2O + 2CO_2$$

Figure D-3. Flow chart for the manufacture of maleic anhydride by catalytic vapor-phase oxidation of benzene.

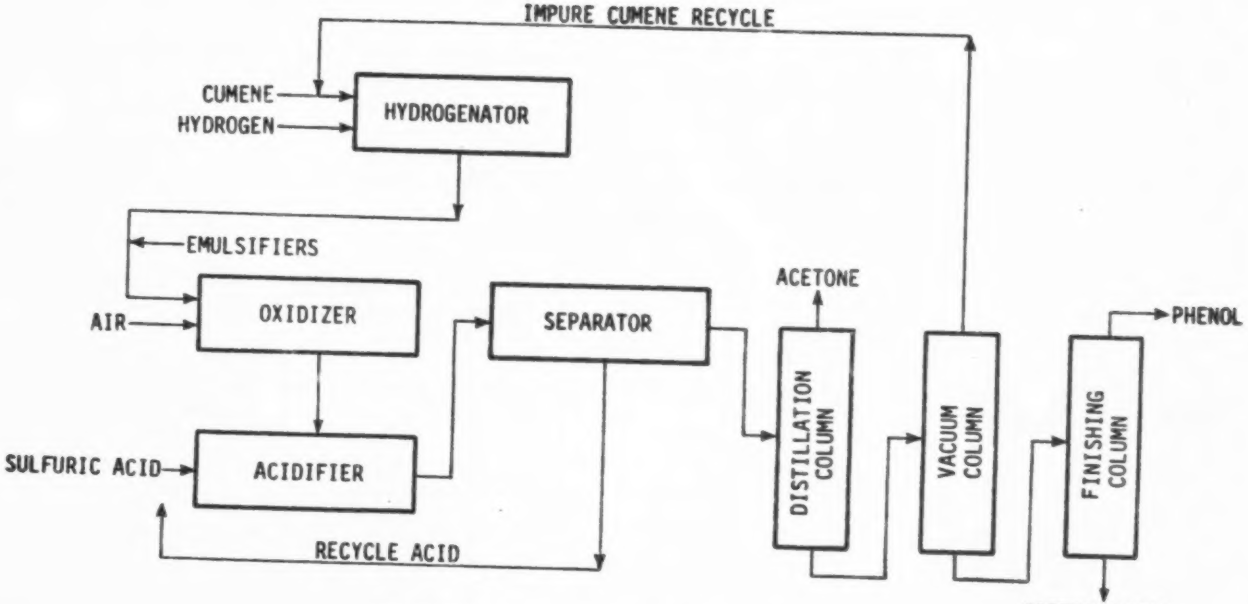
Source: Ref. 59.


FRESH BENZENE
REACTOR
DEPROPANIZER
CONDENSER
BENZENE COLUMN
CONDENSER
RERUN COLUMN
CONDENSER
COMBINED FEED DRUM
CUMENE BOTTOMS
CUMENE
FRESH PROPYLENE PROPANE
PROPANE

$$C_6H_6 + CH_3CH = CH_2 \xrightarrow[\text{SOLID}]{\text{PHOSPHORIC ACID}} C_6H_5CH(CH_3)_2$$

Figure D-4. Process for the manufacture of cumene.

Source: Ref. 81.

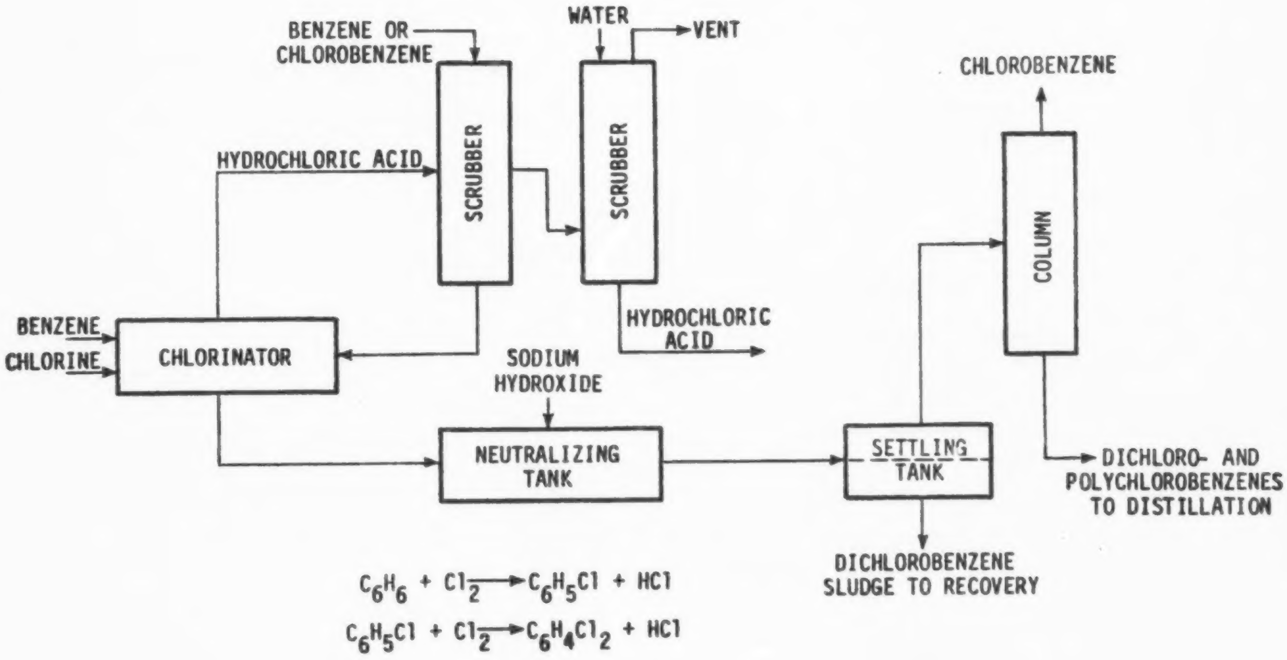

IMPURE CUMENE RECYCLE
CUMENE
HYDROGEN
HYDROGENATOR
EMULSIFIERS
AIR
OXIDIZER
SULFURIC ACID
ACIDIFIER
RECYCLE ACID
SEPARATOR
ACETONE
DISTILLATION COLUMN
VACUUM COLUMN
FINISHING COLUMN
PHENOL
ACETOPHENONE

$$CH_6H_5(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2\ OOH$$

$$C_6H_5C(CH_3)_2\ OOH \longrightarrow C_6H_5OH + (CH_3)_2\ CO$$

Figure D-5. Flow diagram for the manufacture of phenol by the cumene peroxidation process.

Source: Ref. 59.


BENZENE OR CHLOROBENZENE
WATER
VENT
CHLOROBENZENE
HYDROCHLORIC ACID
SCRUBBER
SCRUBBER
COLUMN
BENZENE
CHLORINE
CHLORINATOR
HYDROCHLORIC ACID
SODIUM HYDROXIDE
NEUTRALIZING TANK
SETTLING TANK
DICHLORO- AND POLYCHLOROBENZENES TO DISTILLATION
DICHLOROBENZENE SLUDGE TO RECOVERY

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

$$C_6H_5Cl + Cl_2 \longrightarrow C_6H_4Cl_2 + HCl$$

Figure D-6. Flow diagram for the manufacture of chlorobenzene and by-product dichlorobenzenes.

Source: Ref. 59.

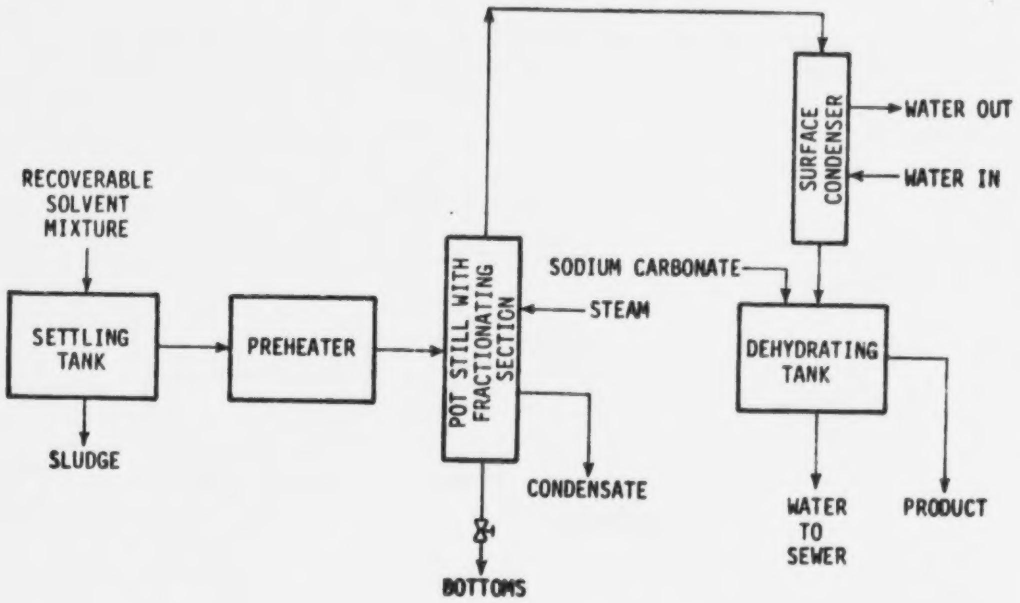

RECOVERABLE SOLVENT MIXTURE
SETTLING TANK
SLUDGE
PREHEATER
POT STILL WITH FRACTIONATING SECTION
STEAM
CONDENSATE
BOTTOMS
SODIUM CARBONATE
SURFACE CONDENSER
WATER OUT
WATER IN
DEHYDRATING TANK
WATER TO SEWER
PRODUCT

Figure D-7. Typical solvent re-refining installation.

Source: Ref. 50.

# APPENDIX E

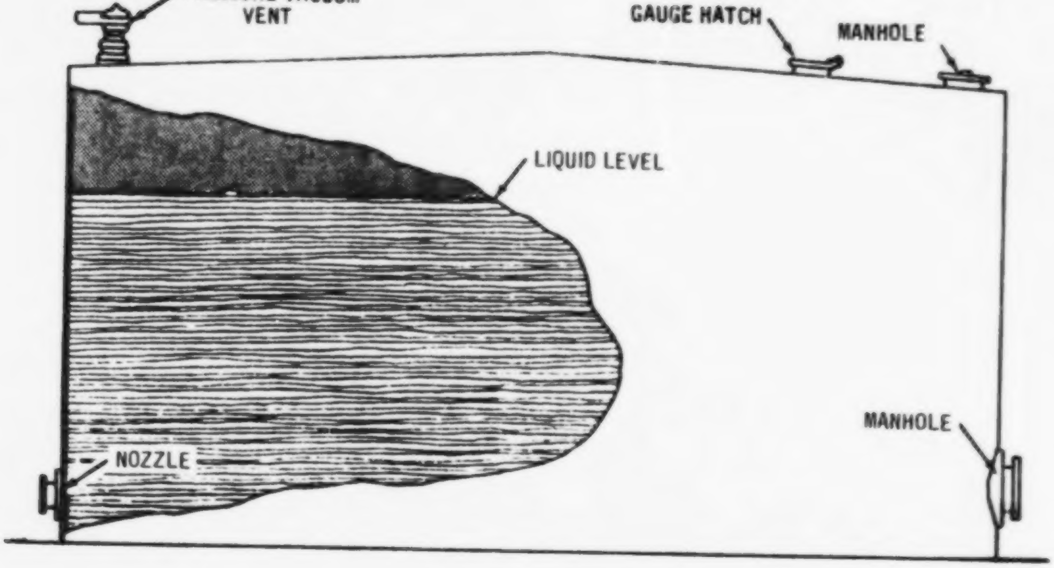

PRESSURE-VACUUM VENT
GAUGE HATCH
MANHOLE
LIQUID LEVEL
MANHOLE
NOZZLE

Figure E-1. Fixed-roof storage tank.
Source: Ref. 29.

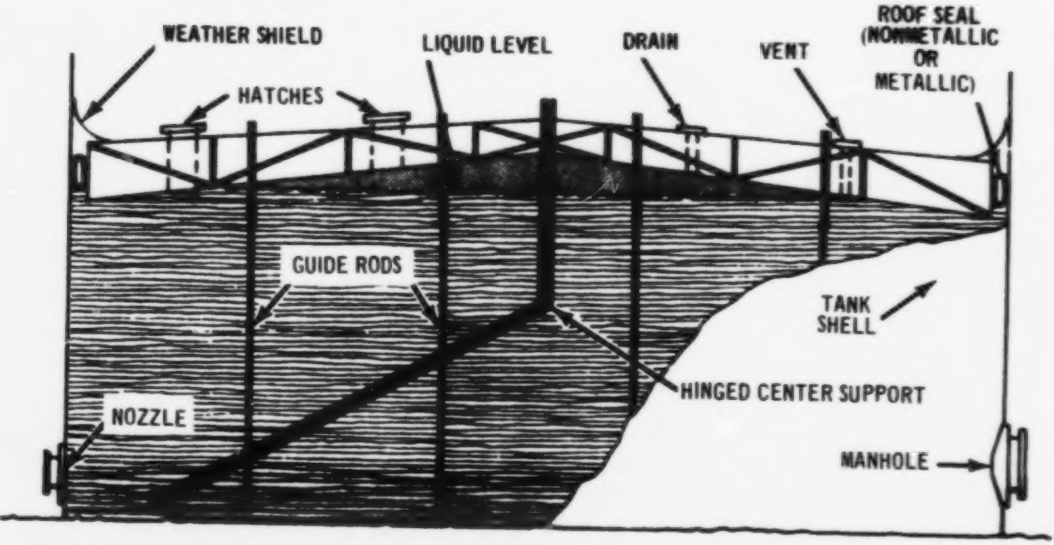

WEATHER SHIELD
HATCHES
LIQUID LEVEL
DRAIN
VENT
ROOF SEAL (NONMETALLIC OR METALLIC)
GUIDE RODS
TANK SHELL
HINGED CENTER SUPPORT
NOZZLE
MANHOLE

Figure E-2. Double-deck floating-roof storage tank (nonmetallic seal).
Source: Ref. 31.

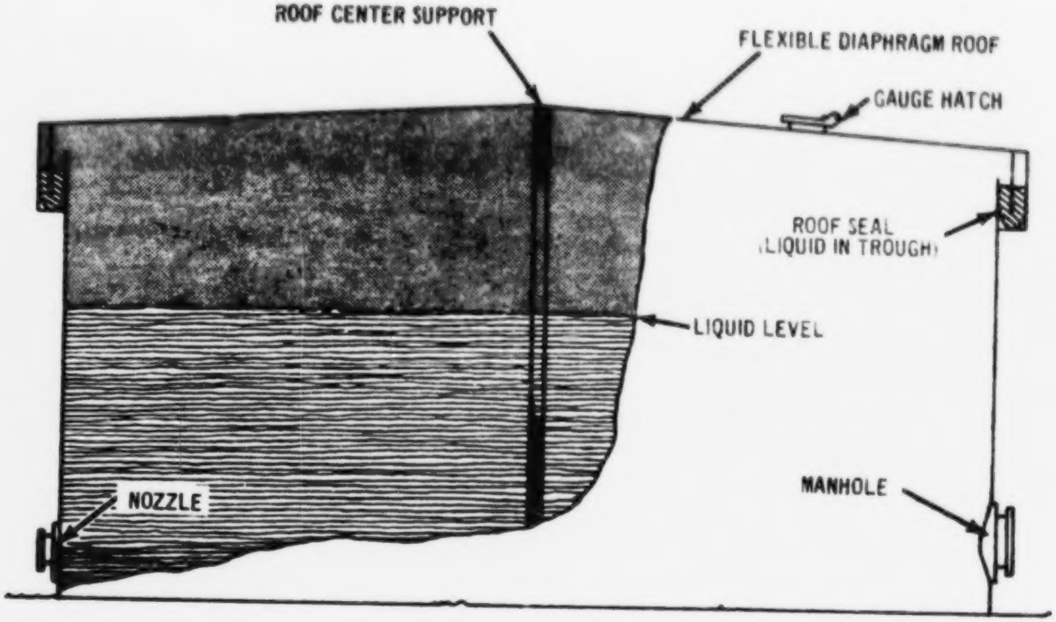

ROOF CENTER SUPPORT
FLEXIBLE DIAPHRAGM ROOF
GAUGE HATCH
ROOF SEAL
(LIQUID IN TROUGH)
LIQUID LEVEL
MANHOLE
NOZZLE

Figure E-3. Variable vapor space storage tank (wet-seal lifter type).
Source: Ref. 31.

PB81 111809

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